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II. Tensile and Flexural Properties

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Manufacturing Chemists Association
Washington, DC

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OUTDOOR PERFORMANCE OF PLASTICS

II. TENSILE AND FLEXURAL PROPERTIES

by
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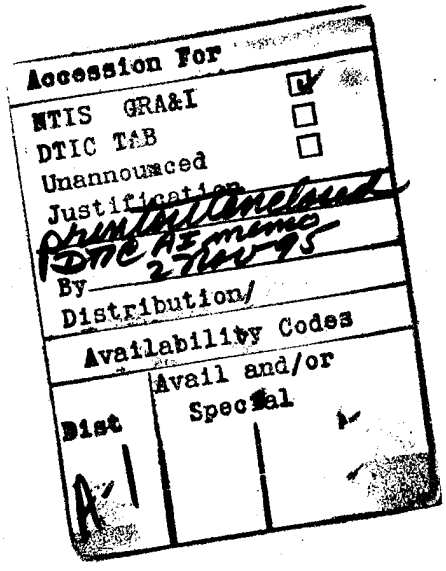

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Outdoor Performance of Plastics. II. Tensile and Flexural Properties,

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Joseph E. Clark, Glenn E. Fulmer, Richard C. Neuman, and James A. Slater.

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Sponsored in part by Manufacturing Chemists Assocation, Washington, DC. Prepared in cooperation with Grace (W.R.) and Co., Clarksville, MD., and Goodrich (B.F.) Chemical Co., Avon Lake, OH. See also Volume 1, PB81-189029, and Volume 3, PB81-189045. Also available in set of 9 reports PC E20, PB81-189011.

This is the second in a series of reports on outdoor performance of 20 plastics. Computer-aided analysis of tensile and flexural strength data is presented for 24-months exposure in Arizona, Florida and Washington, DC. Ultimate elongation (Tensile) and 5% stress (Flexural) showed the greatest change of 11 parameters investigated. These changes characterized loss of elasticity and flexibility. Because of the exponential nature of the deterioration, and objective critical failure-point was defined, by which most of the change had occurred. This is reached at 36.8% retention of initial property-value. Classification systems were useful for quantitatively distinguishing physical performance. Generally, samples, ...

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ABSTRACT

This is the second in a series of reports on outdoor performance of 20 plastics. Computer-aided analysis of tensile and flexural strength data is presented for 24-months exposure in Arizona, Florida and Washington, D. C.

Ultimate elongation (tensile) and 5% stress (flexural) showed the greatest change of 11 parameters investigated. These changes characterized loss of elasticity and flexibility.

Because of the exponential nature of the deterioration, an objective critical failure-point was defined, by which most of the change had occurred. This is reached at 36.8% retention of initial property-value.

Classification systems were useful for quantitatively distinguishing physical performance.

Generally, samples performed worst in Arizona and best in Washington, D. C. Actinic radiation and heat thus appear to be primary agents causing physical degradation.

OUTDOOR PERFORMANCE OF PLASTICS

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APPENDIX 1. EXPONENTIAL NATURE OF PROPERTY-CHANGE

1. OBJECTIVE

The outdoor exposure and testing of 20 plastics in Arizona, Florida, and Washington, D. C. has been completed through 24 months of exposure. This is the second in a series of reports (See NBS Report 9912 for "Introduction and Color Change") on the investigation of eight sets of properties that may be affected by weathering [1]*. Further reports will cover other appearance properties (haze and gloss), as well as properties for early indication of failure (ultraviolet spectra, surface roughness and electrical conductivity). Prediction of a plastic's weatherability is the ultimate goal of the project.

This report deals with the effects of up to 24 months outdoor exposure on tensile and flexural properties of the 20 plastics.

2. INTRODUCTION

Five tensile parameters were measured from the stress-strain curves [2,3] of each plastic (Fig. 1):

(1) Young's Modulus of Elasticity - defined as the ratio of stress (nominal) to corresponding strain below the proportional limit of the plastic. Measurements of tangent modulus were taken as the slope of the tangent to the stress-strain curve, below the stress at 1% strain. (Proportional limit is the greatest stress which a material can sustain without deviation from linear proportionality of stress to strain, i.e., Hooke's Law.)

(2) Yield Stress - defined as the stress at which a plastic exhibits a specified limiting deviation from the proportionality of stress to strain. This was taken as stress at the yield point. (Yield point is the first point on the curve at which an increase in strain occurs without an increase in stress.)

(3) Yield Strain - defined as the strain at the moment the yield point is attained. It corresponds to the point at which the elastic limit is exceeded. (Elastic limit is the greatest stress which a material is capable of sustaining without any permanent strain remaining upon complete release of the stress.)

(4) Failure Stress - defined as the stress at break per unit of original cross-section area. This may or may not be the tensile strength (defined as the maximum stress observed per unit of original cross-section area).

(5) Ultimate Elongation - defined as the maximum elongation, i. e., elongation at failure.

*Figures in brackets are References which are found in the back of this paper.

Six flexural parameters were measured:

(1) Young's Modulus - defined the same way as tensile modulus above.

(2) Yield Stress - defined the same way as tensile yield stress above.

(3) Yield Strain - defined the same way as tensile yield strain above.

(4) Rupture Stress - defined as the stress at which a break occurs for a strain of less than 5%.

(5) Rupture Strain - defined as the strain at which a break occurs for a strain of less than 5%.

(6) 5% Stress - defined as the stress at 5% outer fiber strain (or, stress at 5% strain). Values beyond 5% strain are not considered significant in flexural testing.

3. EXPERIMENTAL

The following twenty plastics under test were described in Part I of this series: polyethylenes (PE), polymethyl methacrylate (PMMA), polyvinyl fluoride (PVF), polyethylene terephthalate (PETP), glass-reinforced polyester (RP), polyvinyl chlorides (PVC).

The plastics were selected to provide a broad representative cross-section of performance. No attempt was made to select the best plastic of any given type. Therefore the results should not be taken to mean that the particular plastic tested is the best possible for that polymeric material.

All 20 plastics were subjected to tensile tests while only the nine 60-mil thick materials (PE, PMMA, RP, PVC's -A, -B, -C, -D, -M and -N) were subjected to flexural tests.

Plots of each of the 5 tensile and 6 flexural parameters as a function of outdoor exposure time were obtained for every plastic, with the aid of the Univac 1108 computer at NBS. Most of the results and conclusions in this report will be based on these graphs.

3.1 Tensile Properties

ASTM D-822-64T (Film)
ASTM D-638-64T (Sheet) with Instron Tensile Tester, Model TTC.

3.1.1 Procedure

Modified ASTM procedures were used by W. R. Grace and Company and B. F. Goodrich Company to measure tensile properties. These tests were run under the supervision of Glenn E. Fulmer and Richard C. Neuman at their respective companies. Poor reproducibility of results from 3-month samples is responsilbe for omission of 3-month data from this report. This imprecision was traced to selection of strain-rates, sample preparation, and slipping in the jaw-grips. More careful cutting of replicates produced improved results, as did selection of elongation-

rates of 2.5%/minute for all samples except some films. Polyethylene, polyvinyl fluoride, and polyethylene terephthalate films were tested at 100%/minute. Slipping from the grips was eliminated almost completely by facing the jaws with "Vellumoid" gasket material.

Three or four replicates were cut from each specimen; seven replicates were run for the original 10-mil PVC-C because it yielded the least reproducible results. This experimental material is probably non-homogeneous.

3.2 Flexural Properties

ASTM D-790-66, with Instron Tensile Tester, Model TTC and Tinius-Olsen 3-point loading flexural jig.

3.2.1 Procedure

The ASTM procedure was used by Glenn E. Fulmer at the Research Division of W. R. Grace & Company to measure flexibility of the 60-mil samples. Each replicate was tested in flexure as a simple beam resting on two supports, and the load applied by means of a loading nose midway between the supports. The specimen was deflected until rupture occurred, or until the maximum fiber strain of 5% was reached, whichever occurred first.

At least 3 replicates were tested at a rate of 0.01 in./in./min. A span-to-depth ratio of 32-to-1 was used.

The sun-exposed side was opposite the loading nose, so that the exposed side was in extension.

3.3 Interpretation of Stress-Strain Curves

The parameters indicated have been used to describe yield and failure points on the curves. Modulus of elasticity is used as an index of stiffness or rigidity of the plastic.

Necessary calculations and data summaries were performed on the IBM 360/30 computer at Research Division, W. R. Grace & Company. In tabulating the properties, average values for each set of replicates are given, and standard deviation, (s).

These properties may be used to quantitatively characterize physical deterioration of the plastic. Surface embrittlement and loss of elongation and flexibility are caused by changes in physical and/or chemical composition. Such changes may result from chemical reactions of the plastic constituents, as well as loss of plasticizer and other additives.

4. RESULTS

Computer plots were prepared for all 5 tensile parameters versus time, and all 6 flexural parameters versus time for each plastic tested. Figures 2 and 3 show these plots for PVC-N. The following observations are based on a study of such graphs for every plastic.

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4.1 Tensile

4.1.1 Tensile Modulus

There is generally very little difference between the initial values of tensile modulus and those up to 24 months although there may be evidence of a cyclic fluctuation of the modulus over time. One-mil and 60-mil polyethylene have the lowest moduli, while PETP and RP have the highest. PVF and PETP show the greatest fluctuation in the measurements over time.

4.1.2 Tensile Yield Stress

This changes very slightly in the course of two years. After two years, the yield stress is slightly higher than its initial value, perhaps an insignificant increase. However, PVC-C (4-mil) and PVC-A (60-mil) increase almost 45% and 35%, respectively. PETP has the highest tensile yield stress and one-mil and 60-mil polyethylene have the lowest.

4.1.3 Tensile Yield Strain

Yield strain decreases very slightly over time for most of the plastics. PVC-A (60-mil) is the only one that increases significantly (52%). One-mil and 60-mil polyethylene have the greatest yield strain.

4.1.4 Failure Stress

Initial failure stress measurements separate the 20 plastics into three groups with the polyethylenes at the low end, the other non-vinyls and polyvinyl fluoride at the high end, and the polyvinyl chlorides in the middle. PETP has the highest failure stress initially and after 24 months of exposure. The polyethylenes have the lowest failure stress at the beginning and after 24 months.

There is no general increase or decrease in failure stress in the plastics: 9 decrease but 6 increase over 2 years while 5 others show no significant change. The latter include 60-mil polyethylene and PMMA. Failure stress also seems to vary in a cyclic manner during the two years.

4.1.5 Ultimate Elongation

Ultimate elongation shows the most rapid degradation of any of the physical properties. Plots of ultimate elongation (Figs. 4-23), with values expressed as percent retention of the initial elongation, exhibit an exponential decay over time. Reinforced polyester and 60-mil polyethylene are exceptions, because their elongation did not change greatly.

In cases in which elongation is a performance criterion, careful judgment must be used since some materials may lose ductility on standing in the dark at room temperature.

The plastics with the lowest initial values for ultimate elongation are PMMA and reinforced polyester. Those with the highest initial values are the polyethylenes. In general, the non-vinyls have the greatest retention of their initial elongations. Polyvinylfluoride has the greatest retention among the vinyls. An increase in ultimate elongation is observed for PMMA, 60-mil polyethylene, reinforced polyester (Arizona only), and 4-mil PVC-A (Washington, D. C. only). All the plastics decrease eventually, except for 1) PMMA and 2) reinforced polyester in Arizona and Florida which is still on the rise at two years. It should also be noted that PMMA is still above its initial value at two years.

A convenient measure of exponential decay is given by the value 1/e (where e = 2.718, the base of natural logarithms). See Appendix 1. For samples exposed in Arizona, 10 of 13 PVC's fall below 1/e, or 37%, of their initial values within six months. At the end of about ten months exposure, all 13 PVC's have fallen below this point. Florida and Washington, D. C. samples also fall to this 37% mark at somewhat longer exposure times.

Changes in retention of initial ultimate elongation must always be referred to the actual values when being interpreted. A comparatively low elongation material such as 10-mil PVC-C may retain the same percentage of its original elongation after one year outdoors as 60-mil polyethylene which is a very high elongation material. Since the polyethylene may be chosen for its high elongation property, a 50% decrease in one year may be extremely significant whereas the same percentage decrease in PVC-C may be totally harmless because of its very low elongation to start with.

4.2 Flexural

4.2.1 Flexural Modulus

Flexural modulus increases during the first six months of exposure for most materials, and then levels off. About half of the materials increase as much as 25-35%, e.g. RP, PVC-A, PVC-B.

Reinforced polyester is initially and after two years the highest modulus material while polyethylene, as expected, has the lowest modulus of the 60-mil materials.

There again seems to be some seasonal oscillatory variation in the modulus over time.

4.2.2 Flexural Yield Stress

Initially, yield stress values increase moderately but then level off in time. Flexural yield stress is higher than tensile yield stress in general.

Data on this parameter were scarce because only 9 materials were thick enough for flexural testing, and some of these did not yield before 5% outer fiber stress. This may be a significant parameter but more data are needed to draw conclusions.

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4.2.3 Flexural Yield Strain

During the first six months of exposure, yield strain decreases slightly, after which it is approximately steady. Flexural yield strain is less than tensile yield strain.

The decrease in yield strain was not great enough to use it as a prime index of physical deterioration.

4.2.4 5% Stress

Eight of the nine plastics show an increase in 5% stress over 6 months (Figs. 24-31). Reinforced polyester, both before and after exposure, is too stiff to strain 5% before rupturing. Of the eight samples, PVC-N and PMMA require the greatest stresses. Polyethylene is again the most flexible, having the lowest values for 5% stress. Increases range from over 100% for PVC-M to about 50% for PVC-N to 10% for PMMA. PVC-M and PMMA eventually decrease at 20 months.

4.2.5 Rupture Stress and Rupture Strain

Data for these two parameters can only be obtained when the sample fails to strain 5%. PMMA, RP, PVC-C, and PVC-N all rupture for most or all exposure times up to two years. Initially PVC-N and PVC-C do not rupture at less than 5% stress.

5. INTERPRETATION OF RESULTS

From the plots and the above observations, it is evident that of the five tensile and six flexural parameters measured, ultimate elongation (Tensile) and 5% stress (Flexural) show the greatest change with time.

It should be noted that some materials showed good physical-property retention, except for ultimate elongation and/or 5% stress. Thus, where elongation is a performance criterion, its initial value and subsequent change are significant. Where elongation is not a performance criterion, other performance parameters should be used.

Ultimate elongation decays rapidly within one year for most of the plastics. 5% stress increases substantially within a short time and then changes little. Changes in both these parameters indicate a loss in elasticity and flexibility, resulting in increasing stiffness and probably brittleness. An increase in 5% stress is generally accompanied by a decrease in ultimate elongation.

In comparing flexural modulus with tensile modulus, it can be seen that flexural modulus is usually higher than tensile modulus for these plastics. This may not be true for all plastics. Our data indicated a possible linear relationship between tensile modulus and flexural modulus.

The effect of weathering on the stress-strain curves can be seen very readily by referring to Figure 1. A slight increase in modulus shifts the curve to the left. The yield point thus moves slightly above and to the left of the initial yield point, raising the yield stress and lowering the yield strain. Since the

ultimate elongation is reduced for most of the plastics, the length of the stress-strain curve is abridged. This does not necessitate a large change in the value for failure stress and is verified by the data which, in fact, vary little. Interpretation of the stress-strain curves of the other plastics can be followed along these same lines of reasoning.

5.1 Classification

With prediction and classification as the goal, percent retention of initial ultimate elongation and retention of initial 5% stress were found to be best suited for this purpose. Either due to insufficient data, or the lack of significant change in the parameter, yield stress, yield strain, rupture stress, and rupture strain were not used for prediction and a classification system.

Flexural modulus and tensile modulus values are grouped closely together for most of the plastics, making it difficult to distinguish performance. Besides this there is comparatively little change in modulus over time for a given plastic. Apparently weather does not affect modulus significantly in a two year period, so modulus would be a poor choice for classifying and predicting performance.

Failure stress also remains the same or near its initial value during two years outdoors for most of the plastics. The 20 plastics group themselves into three sections according to initial and 24-month failure stress. Because of the uncertainty of the data, it is not possible to say more than this about their rankings. PETP, RP, PMMA, and PVF have the highest initial values and maintain their positions after 24 months exposure. Likewise, polyethylene consistently has the lowest values for failure stress. The PVC's continue to fall in between these two groups but ranking the PVC's is impossible due to the large scatter in the data. The changes in failure stress thus do not provide a good means of comparing the outdoor performance of plastics.

Ultimate elongation lends itself very nicely to a classification system and prediction. Initial elongations ranged from 2.6% for reinforced polyester to 814% for 60-mil polyethylene. More importantly, this parameter changes greatly during two years for most of the plastics. Weathering thus has a very significant effect on a plastic's retention of its initial ultimate elongation. Smooth curves drawn in for the samples exposed in Arizona show a definite exponential decrease. This deterioration of ultimate elongation is rapid for PVC's and one-mil polyethylene, and slow for PVF, PETP, and 60-mil polyethylene.

Since weathering in Arizona is due mostly to radiant energy (UV, visible, IR) and is little affected by humidity, rain, and air pollution, the results represent a purer or more ideal case. Discrepancies between the Arizona plots and those of Florida and Washington may be accounted for by the additional environmental factors of moisture and air-pollutants. Due to the exponential nature of these plots, it is convenient to choose the time at which the retention of initial ultimate elongation has reached 1/e (or about 37%) as the critical failure point. This point is reached very early for one-mil polyethylene in Arizona and is not reached within 2 years by reinforced polyester. It can then be said that the polyethylene has failed to retain its physical strength at the end of a few months, while the reinforced polyester has not reached this failure point in two years outdoors. The high failure stress, flexural and tensile modulus of reinforced polyester and the corresponding low values for one-mil polyethylene correlate well with the results of the elongation test.

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5% stress also shows exponential behavior - it increases over time. As in the case of ultimate elongation, 5% stress shows its greatest change within the first 6-12 months, and thereafter varies little. The change is not as great as the change in ultimate elongation but is still very substantial.

5.2 Physical-CLASS Systems

Classification systems based on ultimate elongation and 5% stress were set up. Two systems were constructed for the percent retention of initial ultimate elongation:

1. The first takes advantage of the exponential decay characteristic of the graphs. Three classes were set up (Table 1):

   CLASS 1 - greater than 74% retention ($> 2/e$)

   CLASS 2 - 37%-74% retention ($1/e$ - $2/e$)

   CLASS 3 - less than 37% retention ($< 1/e$)

   CLASS 1 denotes excellent-good weatherability.

   CLASS 2 denotes fair-poor weatherability.

   CLASS 3 denotes a poor material that has failed.

   Based on this system, after two years exposure, 14 of the 19 materials exposed in Arizona have failed, two would be classed as excellent, and the rest are fair. In Florida, 14 of the 19 have failed within two years and in Washington, 10 of 16 exposed materials would be considered failures.

2. A five-class system was set up to allow for greater distinction of the performance of the plastics (Table 2):

   CLASS A - greater than 80% retention

   CLASS B - 60%-80% retention

   CLASS C - 40%-60% retention

   CLASS D - 20%-40% retention, or probable failure.

   CLASS E - less than 20% retention, or failure.

   For the Arizona samples after two years 14 of 19 materials have reached Class E and only two remain as Class A materials. In Florida, 12 of 19 are Class E materials, 2 are Class D, and 2 are Class A after two years. Two year results in Washington put 7 of 16 materials in Class E and 3 in Class D.

- There does not seem to be any great advantage to the second system over the first. By most current standards, Classes D and E can be considered failures and are approximately equivalent to Class 3 of the first system above. Class A and Class 1 are also nearly the same. A "good" plastic is defined by about the same amount of retention in both systems as is a "poor" plastic. The advantage of the first system is that it is set up on the basis of the observed exponential curves and a "failure" point is more logically defined. Mathematical prediction of this failure point is facilitated in system 1.

  One thing that does come out of the second system is that, if by definition A is high and E is low, for every plastic: CLASS (Washington) $\geq$ CLASS (Florida) $\geq$ CLASS (Arizona) after 12 months. The same is true at the end of two years except for PE (60-mil) and RP, i.e., Washington samples degrade slower than Florida samples which degrade slower than Arizona samples.

  A classification system based on the 5% stress data was constructed but was not very successful. Since there were flexural data for only nine of the 20 plastics, and some of the nine plastics ruptured before reaching a value for 5% stress, there are not many data on which to base a classification system. One could be set up and might be satisfactory if extended to more plastics.

  If the three classes of system 1 are used with 5% stress data, most of the measurements fall into Class 2. PVC-B (60-mil) is Class 2 in all locations, PVC-D (60-mil) is Class 3 in Arizona and Florida, while PVC-M is a Class 3 material in all three locations. These results agree well with the corresponding classifications for ultimate elongation retention.

In addition to the three classification systems mentioned above, the plastics can be categorized by the following (Table 3):

(a) Strong vs. weak

(b) Hard vs. soft

(c) Tough vs. brittle

Strong materials have higher failure stress than weak materials; hard or unyielding materials have higher moduli of elasticity; and high elongations indicate a tough material. With the exception of RP, all the plastics became more brittle over two years and more became weaker than stronger. As many became harder as became softer.

5.3 Environmental Factors

From an examination of the graphs and data, there seems to be a correlation between exposure site and change in physical properties. After one year outdoors, the retention of initial ultimate elongation is greatest in Washington, less in Florida, and least in Arizona (See Fig. 10). This is also true after two years exposure outdoors for all samples except PE (60-mil) and RP.

Assuming radiant energy (i.e. actinic radiation and heat) to be the greatest factor in the degradation of plastics, Arizona results can be viewed as the simplest and most severe case. These results are to a good approximation independent of other environmental effects. Thus, Arizona can be used as one standard as a relatively uncomplicated exposure, against which to measure the effects of less intense radiation, humidity, rainfall, and air pollution.

Although actinic radiation and heat appear to be the primary agents causing physical degradation, Washington samples sometimes exhibit a greater loss of physical properties than Florida samples. In other samples Florida values show greater degradation than Washington values. Humidity and rainfall may be important factors here since materials with high water absorption lose strength at high humidities. Furthermore, effects of air pollution should not be overlooked.

6. SUMMARY

This is the second in a series of reports on outdoor performance of 20 plastics. Computer-aided analysis of physical property data is presented. Tensile and flexural strength were measured through 24 months exposure in Arizona, Florida and Washington, D. C. These properties may be used to quantitatively characterize physical deterioration of plastics.

All 20 plastics were subjected to modified ASTM tensile tests, and 5 parameters were measured from the resulting stress-strain curves. The parameters are tangent modulus of elasticity, yield stress, yield strain, failure stress and ultimate elongation.

Only the nine 60-mil thick materials were subjected to ASTM flexural tests. Six parameters were measured from the flexural stress-strain curves. The parameters are tangent modulus, yield stress, yield strain, rupture stress, rupture strain and 5% stress.

Ultimate elongation (Tensile) and 5% stress (Flexural) show the greatest change with time. Ultimate elongation decays rapidly within one year for most of the plastics. 5% stress increases substantially within a short time and then changes little. An increase in 5% stress is generally accompanied by a decrease in ultimate elongation. These changes indicate a loss of elasticity and flexibility, resulting in increasing stiffness and probably brittleness.

Using ultimate elongation and 5% stress, percent retentions of their initial values were found to be useful measures. Either due to insufficient data, or lack of significant change in the parameter, none of the other nine physical-property parameters were nearly as useful.

Smooth curves drawn in for percent retention of initial ultimate elongation show a definite exponential decrease. This deterioration is rapid for PVC's (clear and white-pigmented) and one-mil polyethylene. It is slow for PVF, PETP and 60-mil polyethylene.

5% stress also shows exponential behavior, increasing with time. As in the case of ultimate elongation, 5% stress shows its greatest change within the first 6-12 months, and thereafter varies little.

Due to the exponential nature of the curves, it is feasible to mathematically define a critical failure point, beyond which the property does not change significantly in a short time. This is reached at 36.8% retention of initial value, i.e., the point defined by 1/e, where e is 2.718, the base of natural logarithms.

Classification systems based on ultimate elongation and 5% stress were set up.

There did not seem to be any great advantage of an arbitrary 5-class system over an exponential-based 3-class system; the one based on the 1/e point has mathematical and objective superiority.

Classification based on 5% stress was less successful, because of the scarcity of data. Indications from the available data are that these results agree well with the corresponding classifications for ultimate elongation retention.

Note that generally, the plastics performed worst in Arizona, best in Washington, and intermediate in Florida. Actinic radiation and heat appear to be the primary agents causing physical degradation. However, Washington samples sometimes exhibit a greater loss of physical properties than Florida samples, possibly indicating effects of moisture factors and air pollution.

Keep in mind that these data are for specific formulations of each plastic, and relative performance will not remain the same for all formulations. Likewise, relative rankings vary greatly for different performance properties.

7. RECOMMENDATIONS

Analyses and reporting of these data should be continued and refined.

Objective classification systems such as one described herein should be broadly applied. Application of such mathematically based systems to appearance and other data may provide the foundation for standard criteria of performance, which are badly needed.

Mathematical and statistical description of weathering observations shows promise of being the field's unifying principle. The quantitative approaches of reliability and failure analysis should be applied to weatherability.

8. ACKNOWLEDGMENTS

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9. REFERENCES

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[2] 1968 Book of ASTM Standards, Part 27, American Society for Testing and Materials, Philadelphia.

[3] "Engineering Properties and Applications of Plastics", Gilbert F. Kinney, Wiley Publishers (1957).

APPENDIX 1

EXPONENTIAL NATURE OF PROPERTY-CHANGE

Study of the graphs herein revealed that the physical properties which changed significantly appeared to follow exponential decay curves. Many similar curves may be found in the literature to support this observation. Furthermore, the color-changes detailed in our earlier NBS Report #9912 exhibit similar nature.

A relatively simple expression can be written to describe this behavior quantitatively:

$$y = Ae^{-Bt^n} + C$$

where A, B, C and n are constants to be determined for each plastic in a given exposure, t is time, and y is the property under study.

Note the similarity between this exponential and the exponentials describing chemical kinetics [A]. Kinetic equations describe changes in concentration of reacting substances by equations such as:

$$y = A(1 - e^{-Kt})$$

where y is concentration of the reaction-product at time t, A is initial concentration of reactant, and k is the "rate constant".

In addition, exponential equations have recently begun to appear in publications on weathering. Especially significant is the equation of Kamal & Saxon [B]:

$$y = Ae^{B(t-c)}$$

where y is the value of property measured at time t, and A, B, and C are constants. The constants were found to be dependent on exposure parameters for 10 plastics and 13 properties in accelerated "wet" xenon exposures.

See also the equation of Daiger & Madson [C]:

$$y = K - Ae^{-Bt^2}$$

where y is red-reflectance of paints at time t, and k, A, and B are constants. This equation led to a current duPont method for evaluating paints.

Since the graphs commonly appear to have this form, it is desirable and possible to choose an arbitrary failure-point on the curves. Furthermore, Figure 32 indicates that there is a point common to various exponential curves. This exists at the value, 1/e, where e = 2.718, the base of natural logarithms:

$$\frac{1}{e} = \frac{1}{2.718} = 0.368$$

This critical value appears in several interesting, and apparently unrelated, places in scientific and engineering literature. It is often useful as the point beyond which the variant does not change significantly with time.

Example 1. In analysis of bearing fatigue data and automotive parts failure [D], the fraction (F) of parts that failed within N cycles is

$$F = 1 - \exp\left[-\left(\frac{N}{L}\right)^{B}\right]$$

where L is called the "characteristic life", the number of cycles at which 63.2% (1 - .368) of all the samples will have failed.

Example 2. In the theory of good electrical conductors [E], the "skin depth" (d) is defined as the depth within the conductor at which the current-density falls to 1/e of its value at the surface of the conductor. In other words, most of the current flows within a layer of thickness d.

Example 3. In electronic circuit theory [F], the pulse that is produced from an R-C circuit is of the form $y=\exp(-t/RC)$. A critical time, or time constant, for the circuit is defined for $t = RC$, that is, for the value $e^{-1} = 1/e$.

In deterioration of plastics, it is sensible to similarly define a failure-point mathematically and objectively. It is a most significant bonus that, beyond this 1/e value, the measured property does not change significantly with time.

Appendix References:

[A] "Chemical Kinetics", Keith J. Laidler, McGraw-Hill, N.Y. (1950).

[B] "Analysis & Prediction of Weatherability", M.R. Kamal & R. Saxon, Applied Polymer Symposia, No. 4, 1-28 (1967).

[C] W. H. Daiger and W. H. Madson, J. of Paint Technology, 39, 399-410 (1967).

[D] "Weibull Plot Predicts Fatigue Life", L. G. Johnson, J. of Society of Automotive Engineers, 70, 67-68 (1962).

[E] "Classical Dynamics of Particles & Systems", J. B. Marion, Academic Press, N. Y. (1965).

[F] "Electronics", A. O. Williams, Jr., Van Nostrand Company, N. Y. (1953).

LIST OF TABLES

Table	
1	Classification System I: Exponential
2	Classification System II: 5 Equal Classes
3	Change in Tensile Properties Over Two Years in Arizona

TABLE 1

CLASSIFICATION SYSTEM I: EXPONENTIAL

Class	Arizona		Florida		Washington, D. C.	
	1 Year	2 Years	1 Year	2 Years	1 Year	2 Years
1	PE-60 PMMA-60 PETP-5 RP-60	PMMA-60 RP-60	PE-60 PMMA-60 PETP-5 RP-60	PMMA-60 RP-60	PE-60 PMMA-60 PETP-5 RP-60 PVC-A4 PVC-D4	PE-60 PMMA-60 RP-60
2	PVF-1	PE-60 PVF-1 PETP-5	PVF-1 PVC-B4 -B10 PVC-A4 PVC-D10	PVF-1 PETP-5 PVC-D10	PVF-1 PVC-B4 -B60 PVC-A60 PVC-M60	PVF-1 PETP-5 PVC-A4
3	PE-1[a] PVC-B4 -B10 -B60 PVC-C4 -C10 -C60 PVC-N60 PVC-A4 -A10 PVC-D4 -D10 -D60 PVC-M60	PE-1[a] PVC-B4 -B10 -B60 PVC-C4[b] -C10 -C60[c] PVC-N60 PVC-A4 -A10 PVC-D4 -D10 -D60 PVC-M60	PE-1[a] PVC-B60 PVC-C4 -C10 -C60 PVC-N60 PVC-A10 PVC-D4 -D60 PVC-M60	PE-1[a] PE-60 PVC-B4 -B10 -B60 PVC-C4[b] -C10 -C60[c] PVC-N60 PVC-A4 -A10 PVC-D4 -D60 PVC-M60	PE-1 PVC-C4 -C60[c] PVC-N60 PVC-D60	PE-1 PVC-B4 -B60 PVC-C4 -C60[c] PVC-N60 PVC-A60 PVC-D4 -D60 PVC-M60

[a]Classification of PE-1 is based on 6 month data in Arizona and 9 month data in Florida.

[b]Classification of PVC-C4 is based on 12 month data in Arizona and Florida.

[c]Classification of PVC-C60 is based on 12 month data in Arizona and Florida and 9 month data in Washington, D. C.

TABLE 2

CLASSIFICATION SYSTEM II: 5 EQUAL CLASSES

Class	Arizona		Florida		Washington, D. C.	
	1 Year	2 Years	1 Year	2 Years	1 Year	2 Years
A	PE-60 PMMA-60 PETP-5 RP-60	PMMA-60 RP-60	PE-60 PMMA-60 PETP-5 RP-60	PMMA-60 RP-60	PE-60 PMMA-60 PETP-5 RP-60 PVC-A4	PE-60 PMMA-60
B	PVF-1	PETP-5	PVF-1	PVF-1 PETP-5	PVF-1 PVC-B4 PVC-D4	PVF-1 PETP-5 RP-60
C		PE-60 PVF-1	PVC-B4 -B10 PVC-A4 PVC-D10	PVC-D10	PVC-A60 PVC-M60	PVC-A4
D			PVC-B60 PVC-A10 PVC-D4 -D60 PVC-M60	PE-60 PVC-M60	PVC-B60 PVC-N60 PVC-D60	PVC-B4 -B60 PVC-M60
E	PE-1[a] PVC-B4 PVC-B10 -B60 PVC-C4 -C10 -C60 PVC-N60 PVC-A4 -A10 PVC-D4 -D10 -D60 PVC-M60	PE-1[a] PVC-B4 -B10 -B60 PVC-C4[b] -C10 -C60[c] PVC-N60 PVC-A4 -A10 PVC-D4 -D10 -D60 PVC-M60	PE-1[a] PVC-C4 -C10 -C60 PVC-N60	PE-1[a] PVC-B4 -B10 -B60 PVC-C4[b] -C10 -C60[c] PVC-N60 PVC-A4 -A10 PVC-D4 -D60	PE-1 PVC-C4 -C60[c]	PE-1 PVC-C4 -C60[c] PVC-N60 PVC-A60 PVC-D4 -D60

[a]Classification of PE-1 is based on 6 month data in Arizona and 9 month data in Florida.

[b]Classification of PVC-C4 is based on 12 month data in Arizona and Florida.

[c]Classification of PVC-C60 is based on 12 month data in Arizona and Florida and 9 month data in Washington, D. C.

TABLE 3

CHANGE IN TENSILE PROPERTIES

OVER TWO YEARS IN ARIZONA*

Plastic	Stronger (Failure Stress)	Weaker (Failure Stress)	Harder (Modulus)	Softer (Modulus)	Tougher (Ultimate Elongation)	Brittler (Ultimate Elongation)
PE-1		X[1]		X[1]		X[1]
PE-60		NC[2]		NC		X
PMMA-60		NC	X			X
PVF-1		X		NC		X
PETP-5		NC[3]		X		X
RP-60	X		X		X	
PVC-B4		X		NC		X
-B10		X		NC		X
-B60		X	X			X
PVC-C4	X[4]		X[4]			X[4]
-C10		X[3]	X			X
-C60	X[4]			X[4]		X[4]
PVC-N60	X			X		X
PVC-A4		X[3]		X		X
-A10		NC[3]	X			X
-A60	(X)[5]			(X)[5]		(X)[5]
PVC-D4		X		NC		X
-D10	X		X			X
-D60		NC		NC		X
PVC-M60		X		X		X

[1]Change at 6 months.

[2]NC = No significant change.

[3]Values for failure stress increase initially then decrease to original value or below at 24 months.

[4]Change at 12 months

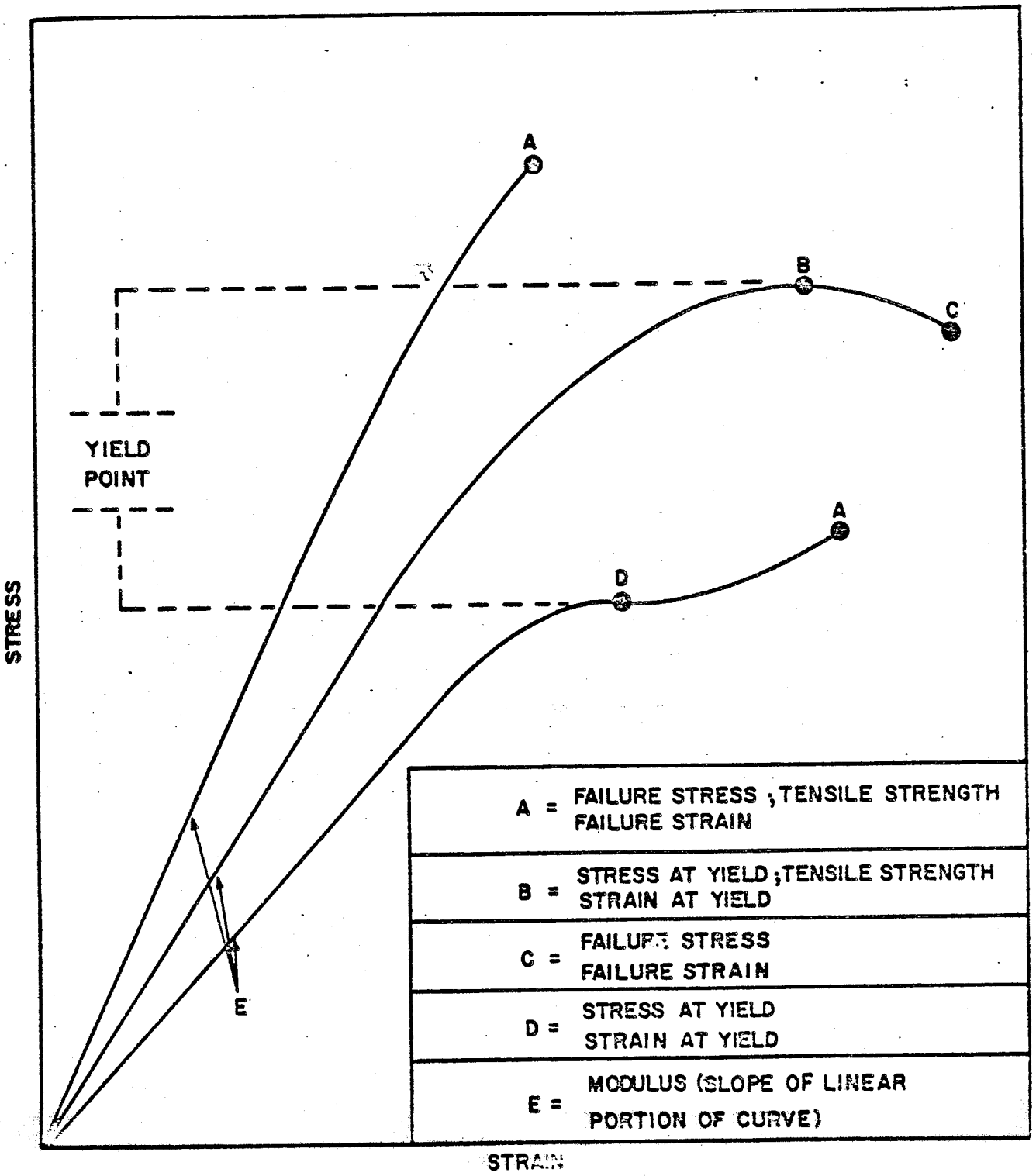
[5]Washington valu

*Classification system adopted from Kinney, Engineering Properties and Applications of Plastics.

LIST OF GRAPHS

Figure	
1	Typical Stress-Strain Curves
2	Tensile Property Change vs. Time For PVC-N
3	Flexural Property Change vs. Time For PVC-N
4	Ultimate Elongation - Polyethylene (one mil)
5	" " - Polyethylene (60 mil)
6	" " - Polymethyl Methacrylate (60 mil)
7	" " - Polyvinyl Fluoride (one mil)
8	" " - Polyethylene Terephthalate (5 mil)
9	" " - Glass-Reinforced Polyester (60 mil)
10	" " - Polyvinyl Chloride-B (4 mil)
11	" " - " " -B (10 mil)
12	" " - " " -B (60 mil)
13	" " - " " -C (4 mil)
14	" " - " " -C (10 mil)
15	" " - " " -C (60 mil)
16	" " - " " -N (60 mil)
17	" " - " " -A (4 mil)
18	" " - " " -A (10 mil)
19	" " - " " -A (60 mil)
20	" " - " " -D (4 mil)
21	" " - " " -D (10 mil)
22	" " - " " -D (60 mil)
23	" " - " " -M (60 mil)
24	5% Stress - Polyethylene (60 mil)
25	" " - Polymethyl Methacrylate (60 mil)
26	" " - Polyvinyl Chloride-B (60 mil)
27	" " - " " -C (60 mil)
28	" " - " " -N (60 mil)
29	" " - " " -A (60 mil)
30	" " - " " -D (60 mil)
31	" " - " " -M (60 mil)
32	Plots of $Y = e^{-t^n}$

FIGURE 1



TENSILE DESIGNATIONS

FIGURE 2

TENSILE PROPERTY CHANGE vs. TIME IN MONTHS

PVC-N (60 MILS)

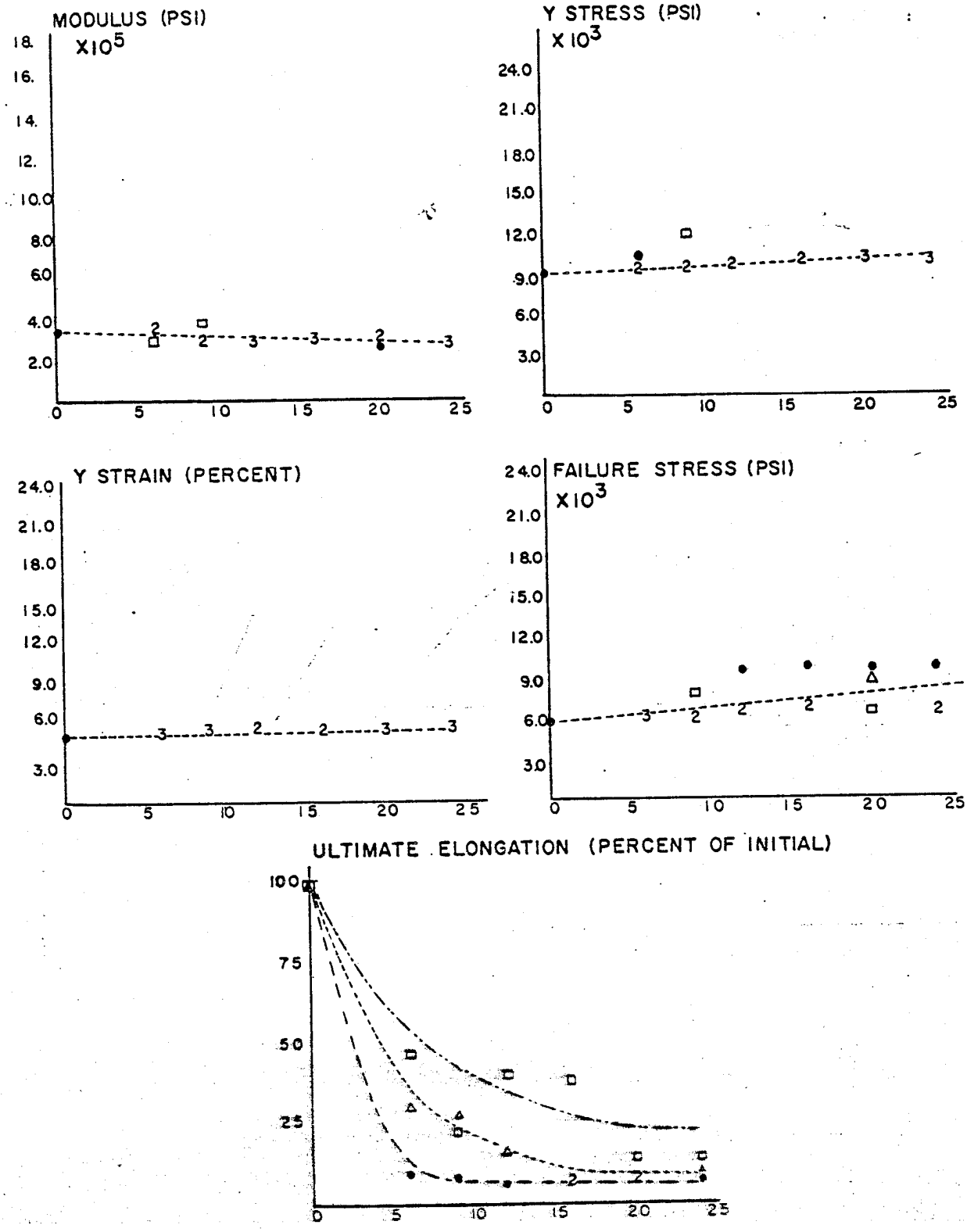


FIGURE 3

FLEXURAL PROPERTY CHANGE vs. TIME IN MONTHS

PVC-N (60 MILS)

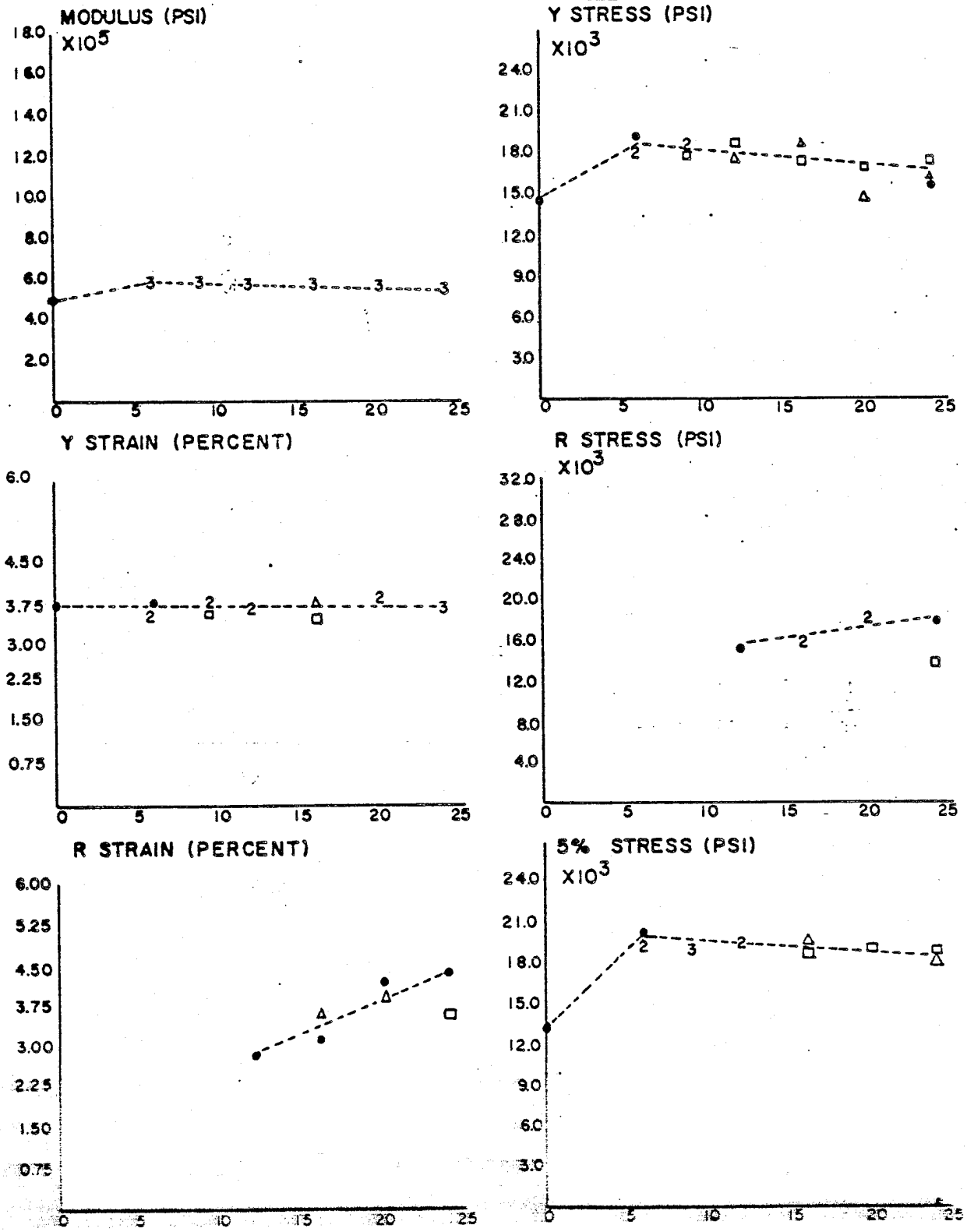
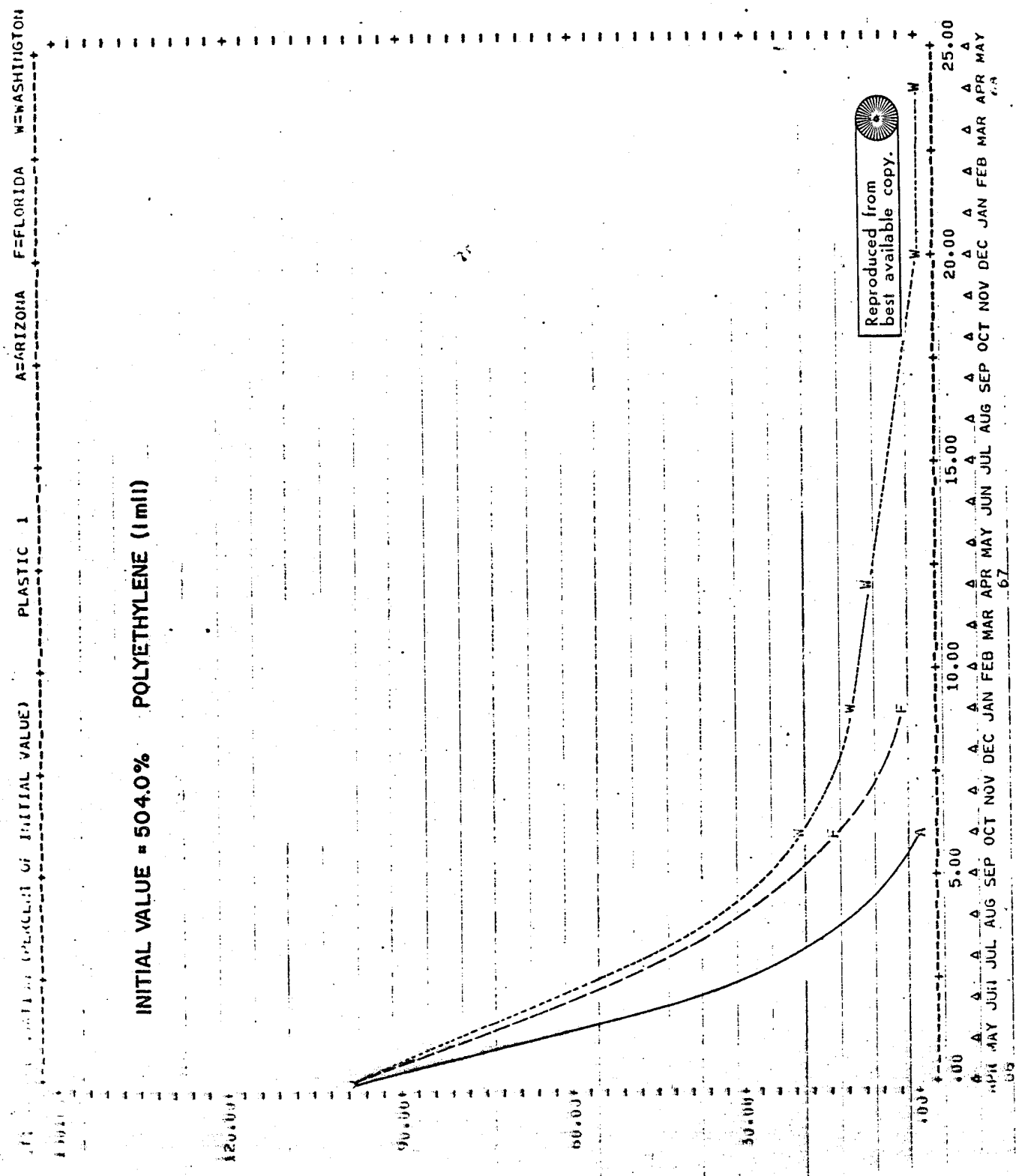


FIGURE 4


A=ARIZONA F=FLORIDA W=WASHINGTON
PLASTIC 1
INITIAL VALUE = 504.0%
POLYETHYLENE (1mil)
Reproduced from best available copy.
5.00
10.00
15.00
20.00
25.00
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY

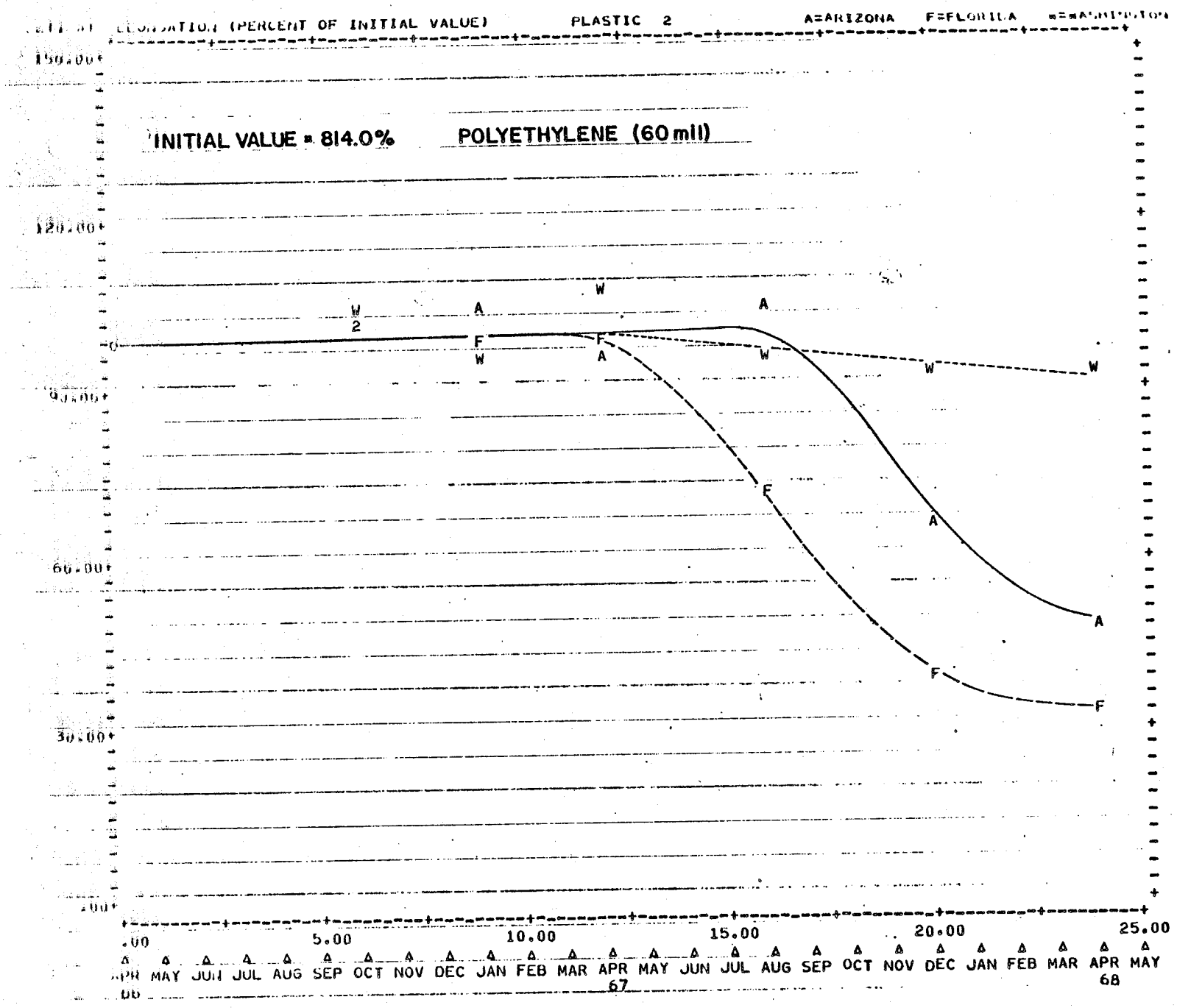
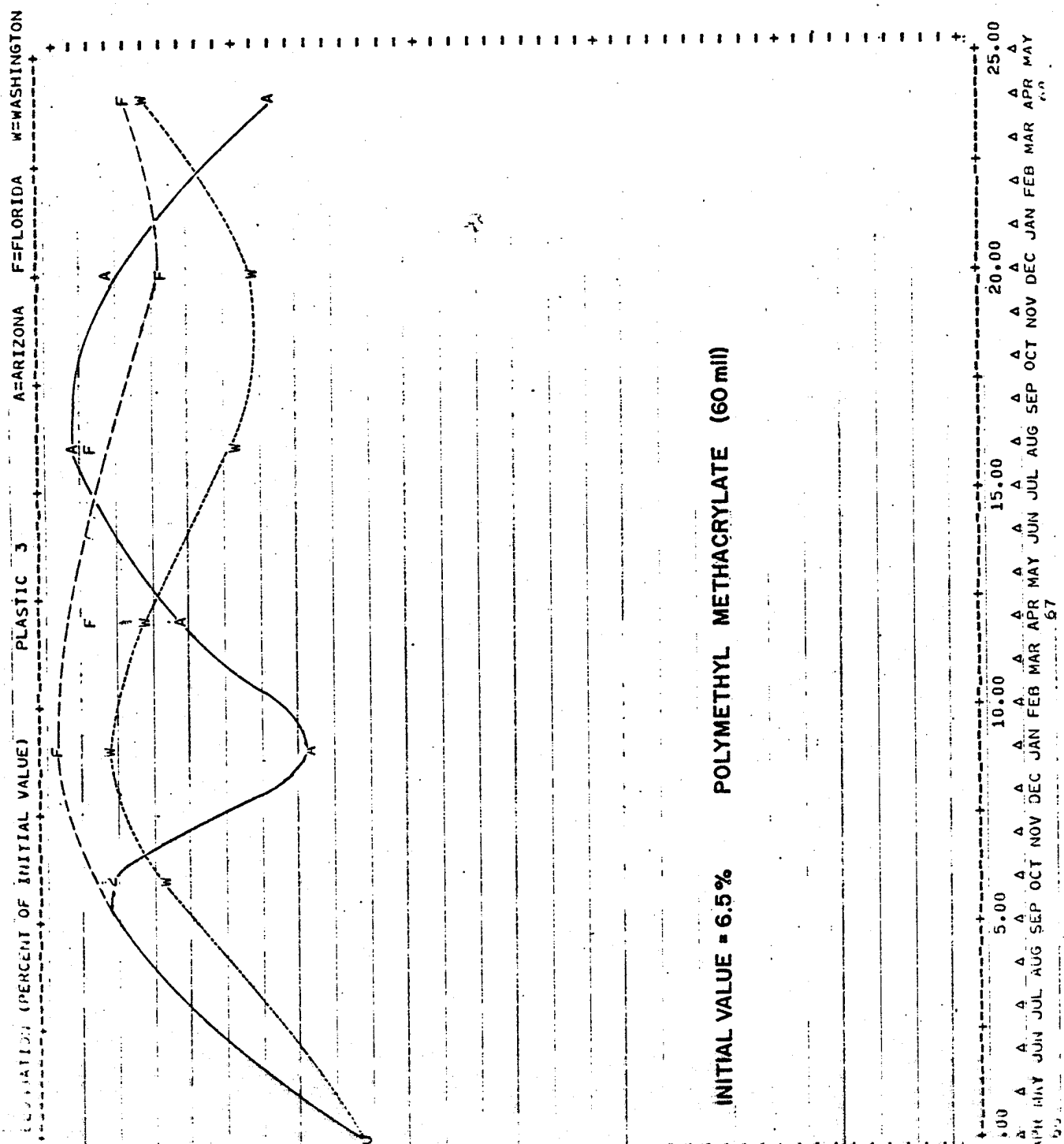

PLASTIC 2
A=ARIZONA F=FLORIDA
INITIAL VALUE = 814.0%
POLYETHYLENE (60 mil)
150.00
120.00
60.00
30.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
66
67
68

FIGURE 5

FIGURE 6


A=ARIZONA F=FLORIDA W=WASHINGTON
PLASTIC 3
INITIAL VALUE = 6.5%
POLYMETHYL METHACRYLATE (60 mil)
120.00
90.00
60.00
30.00
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
67

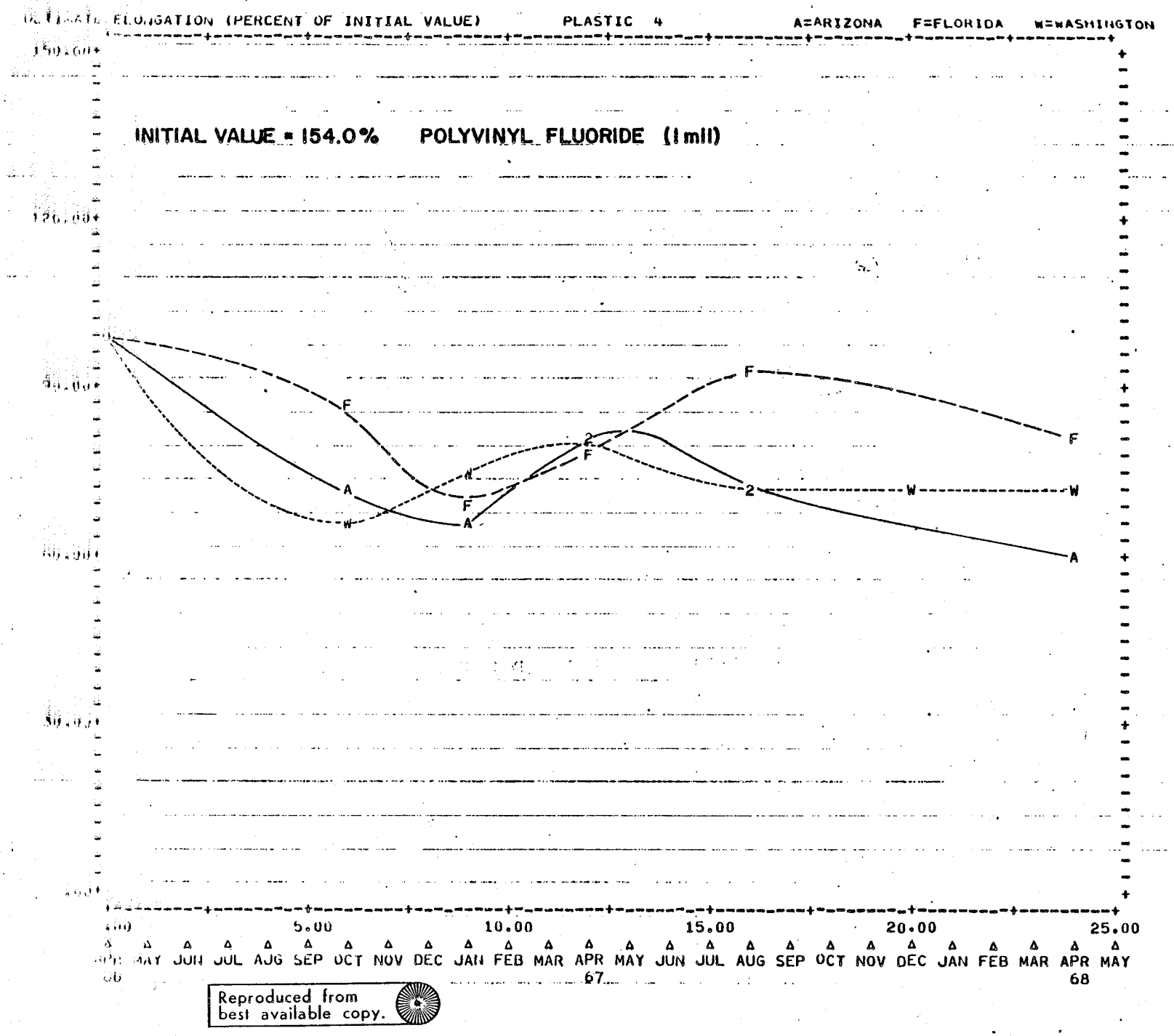


FIGURE 7

Reproduced from best available copy.

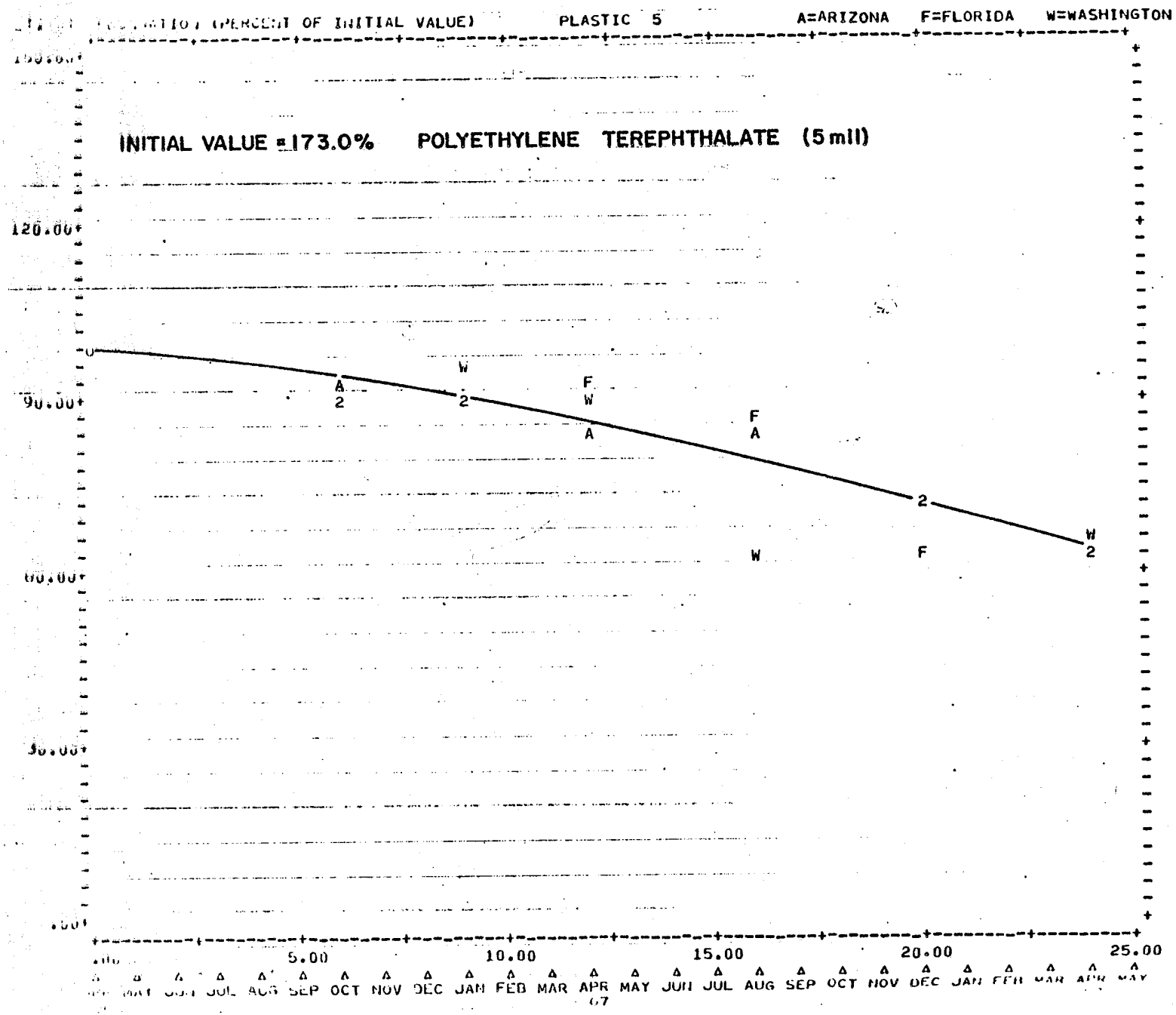
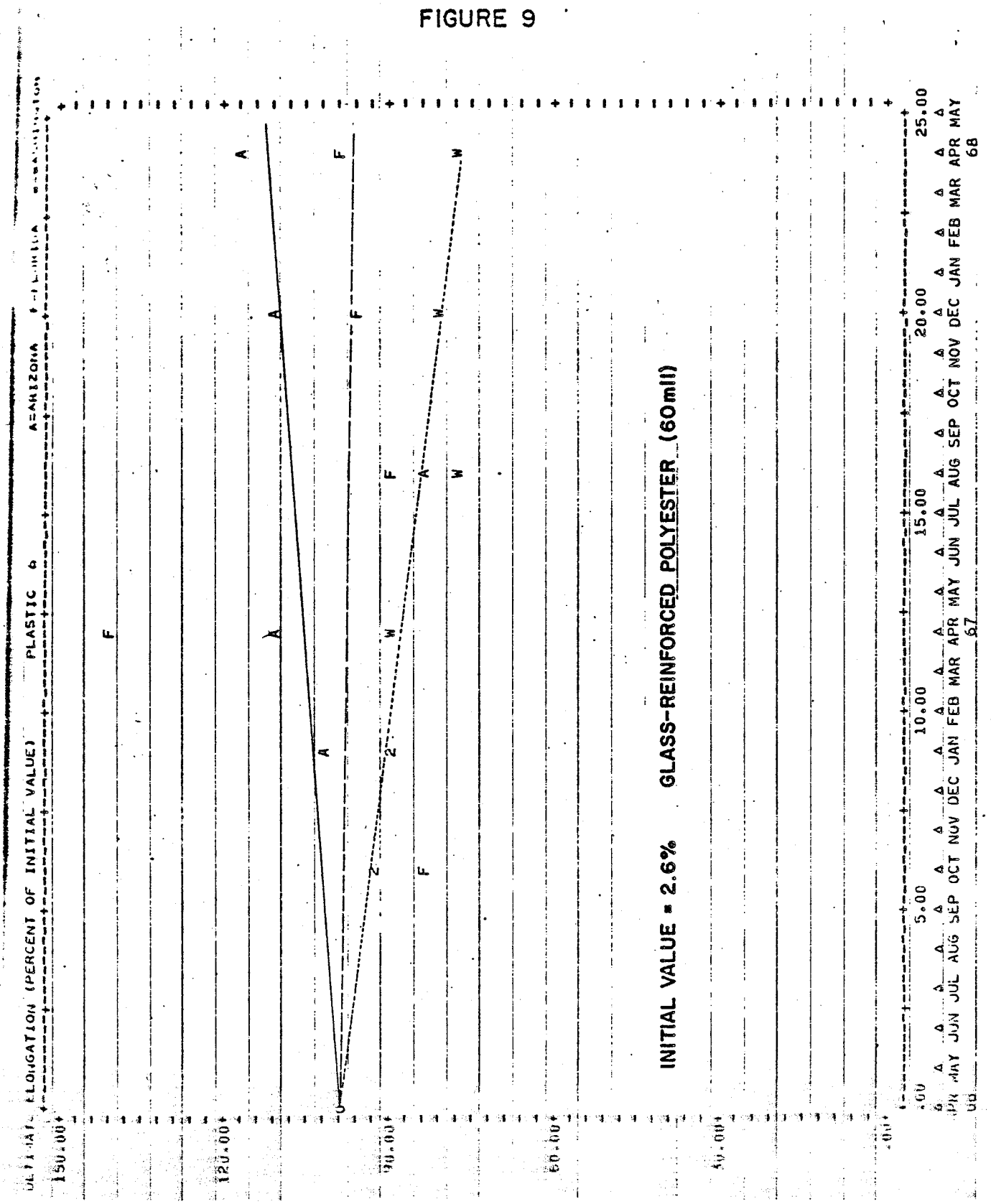

PLASTIC 5
A=ARIZONA F=FLORIDA W=WASHINGTON
INITIAL VALUE =173.0% POLYETHYLENE TEREPHTHALATE (5 mil)
120.00
90.00
60.00
5.00
10.00
15.00
20.00
25.00
MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
67

FIGURE 8

FIGURE 9


ELONGATION (PERCENT OF INITIAL VALUE)
PLASTIC 6
ARIZONA
150.00
120.00
90.00
60.00
30.00
0.00
INITIAL VALUE = 2.6%
GLASS-REINFORCED POLYESTER (60mil)
5.00
10.00
15.00
20.00
25.00
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
67
68

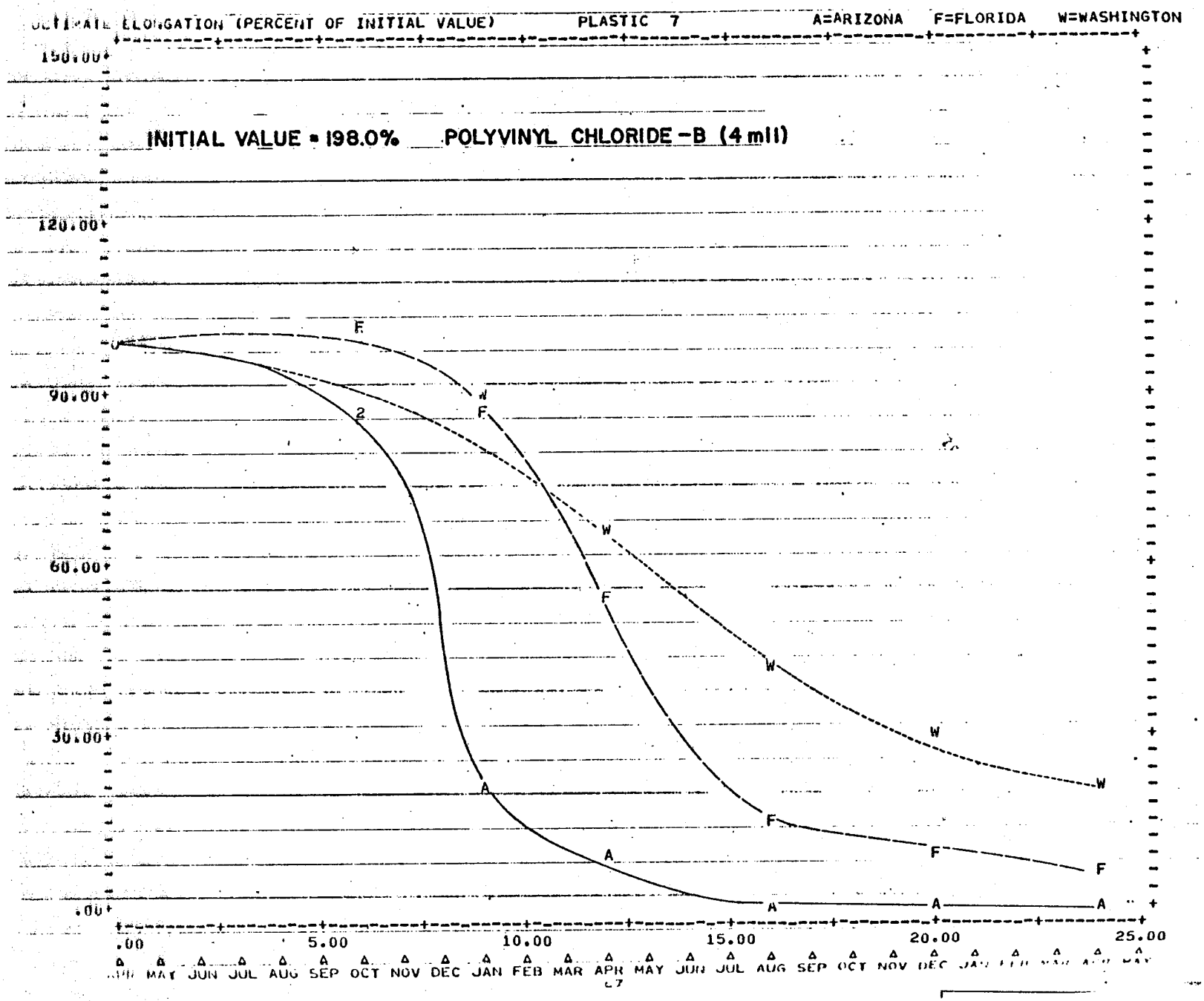

ULTIMATE ELONGATION (PERCENT OF INITIAL VALUE)
PLASTIC 7
A=ARIZONA F=FLORIDA W=WASHINGTON
INITIAL VALUE = 198.0% POLYVINYL CHLORIDE-B (4 mil)
150.00
120.00
90.00
60.00
30.00
.00
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
'67

FIGURE 10

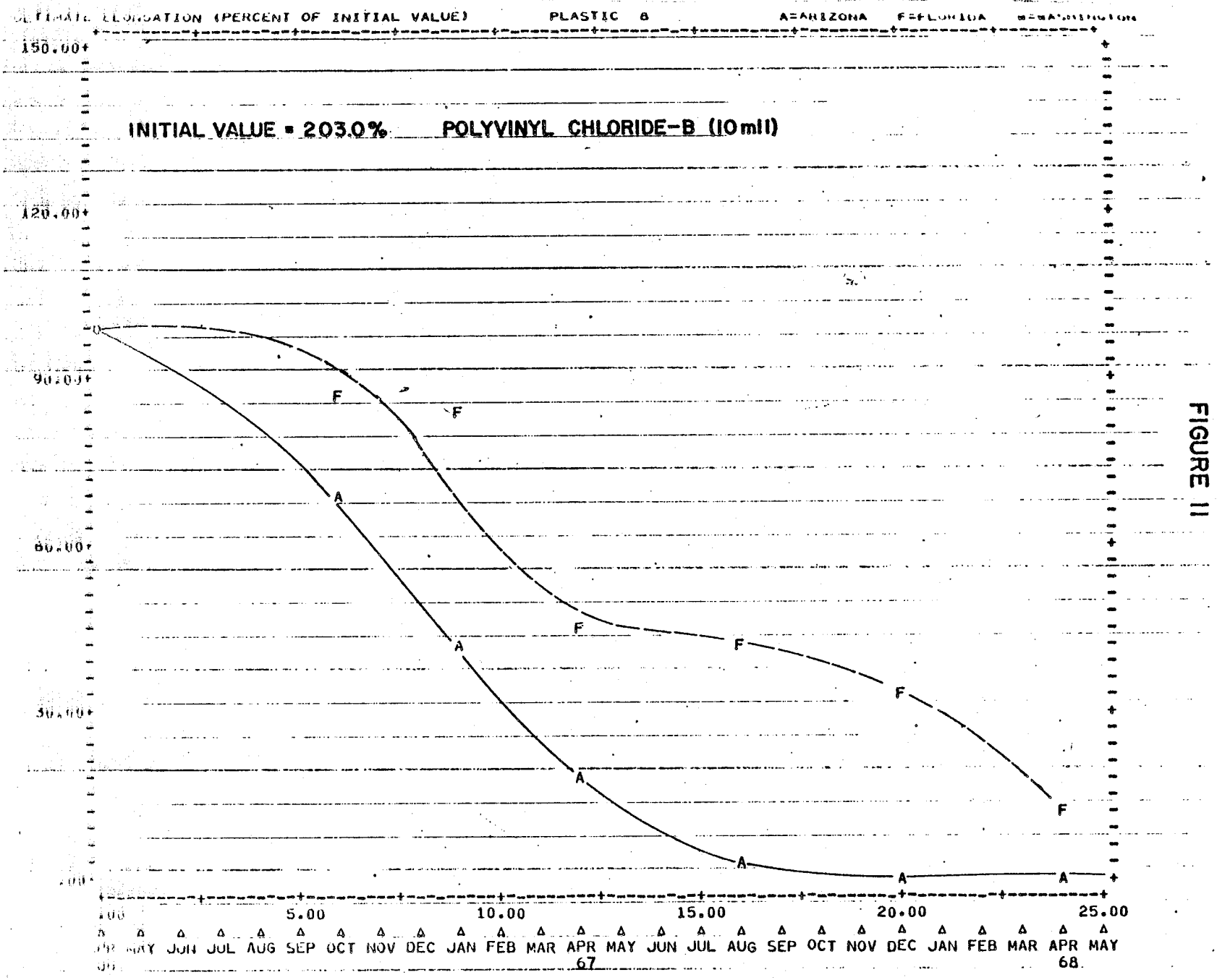
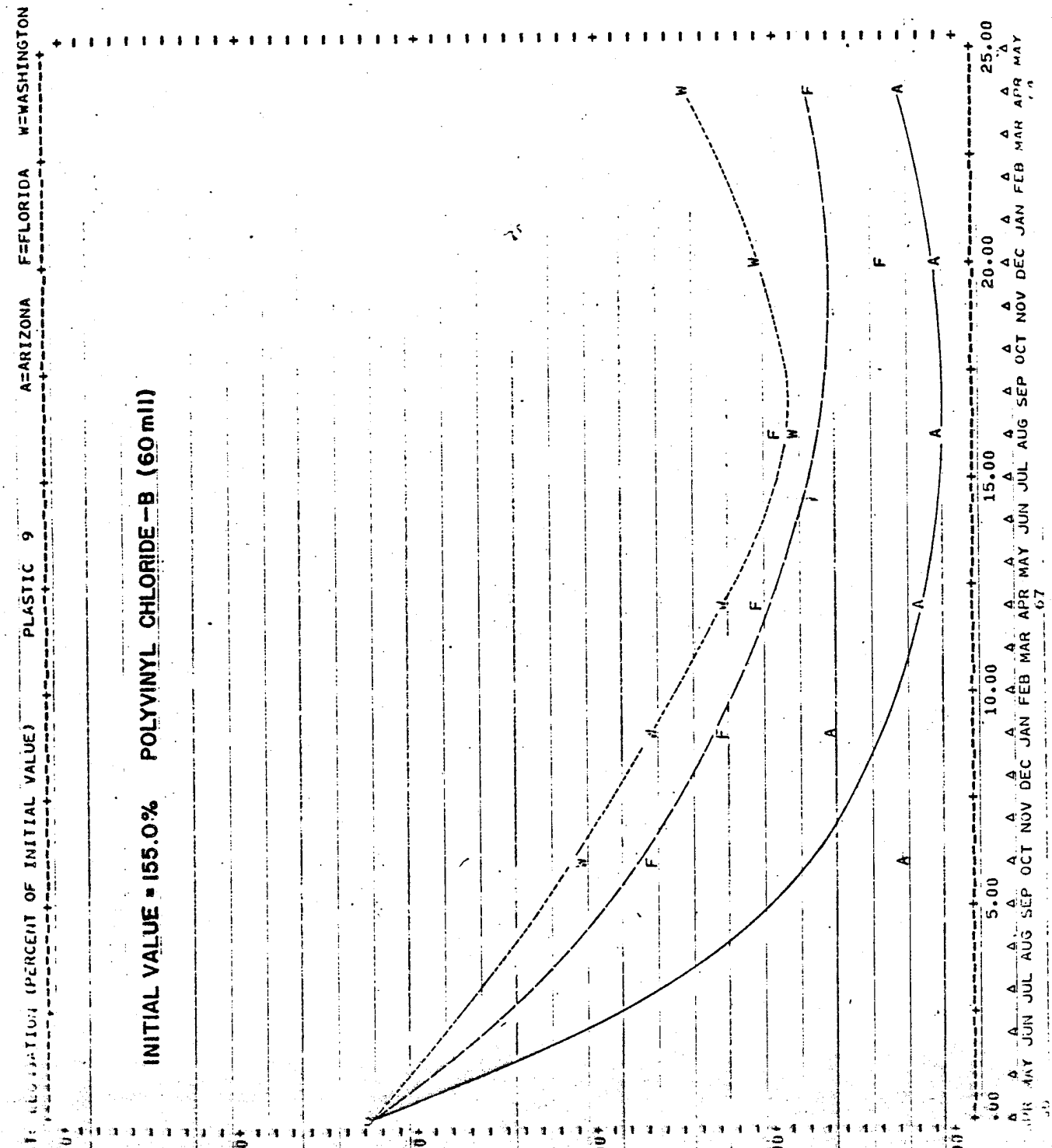

ULTIMATE ELONGATION (PERCENT OF INITIAL VALUE)
PLASTIC B
A=ARIZONA F=FLORIDA
INITIAL VALUE = 203.0%
POLYVINYL CHLORIDE-B (10 mil)
150.00
120.00
90.00
60.00
30.00
0
5.00
10.00
15.00
20.00
25.00
MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
67
68

FIGURE II

FIGURE 12


A=ARIZONA F=FLORIDA W=WASHINGTON
PLASTIC 9
INITIAL VALUE = 155.0% POLYVINYL CHLORIDE-B (60 mil)
150.00
125.00
90.00
60.00
30.00
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
67

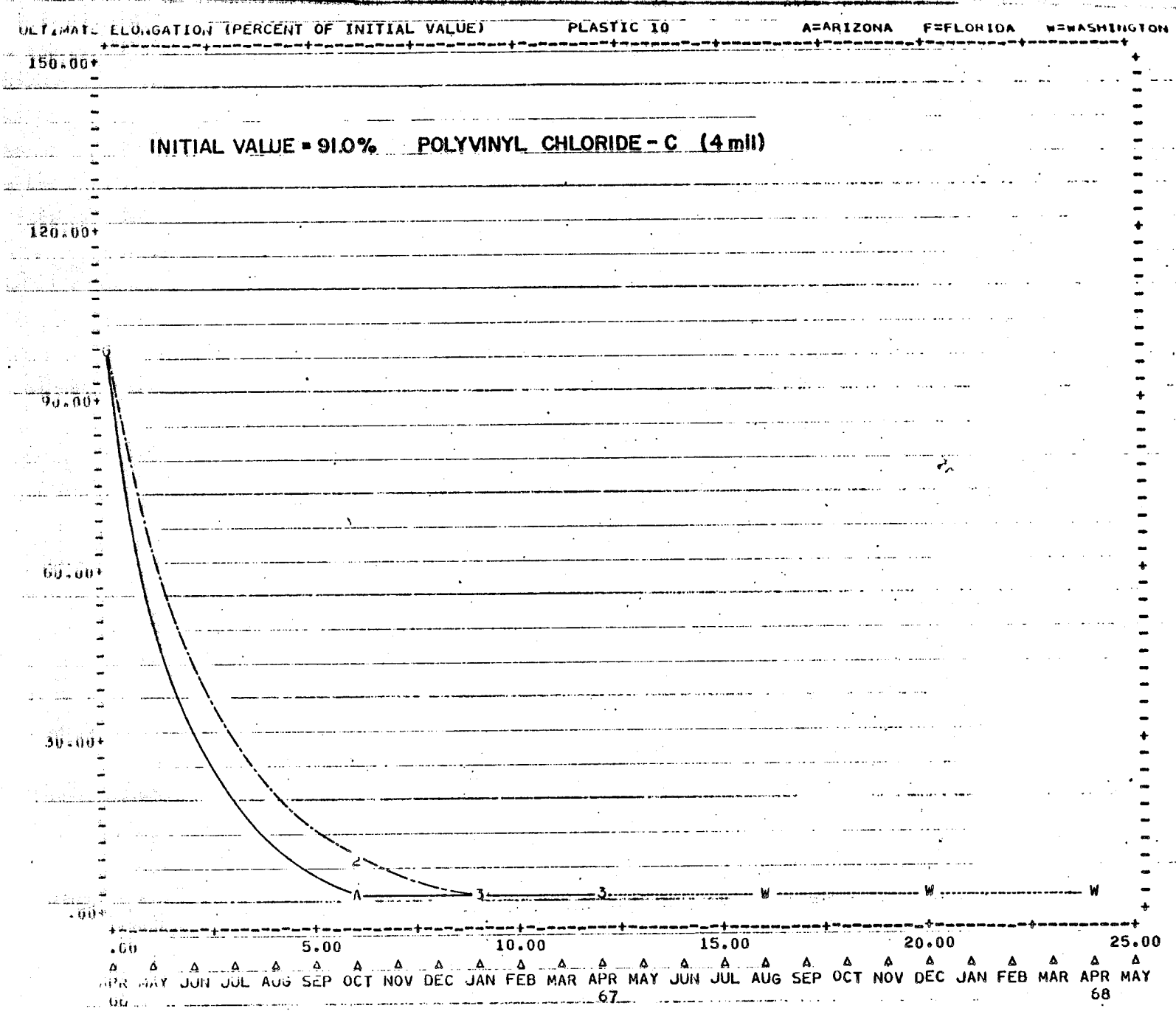

ULTIMATE ELONGATION (PERCENT OF INITIAL VALUE)
PLASTIC 10
A=ARIZONA F=FLORIDA W=WASHINGTON
150.00
120.00
90.00
60.00
30.00
.00
INITIAL VALUE = 91.0% POLYVINYL CHLORIDE - C (4 mil)
A
F
W
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
66
67
68

FIGURE 13

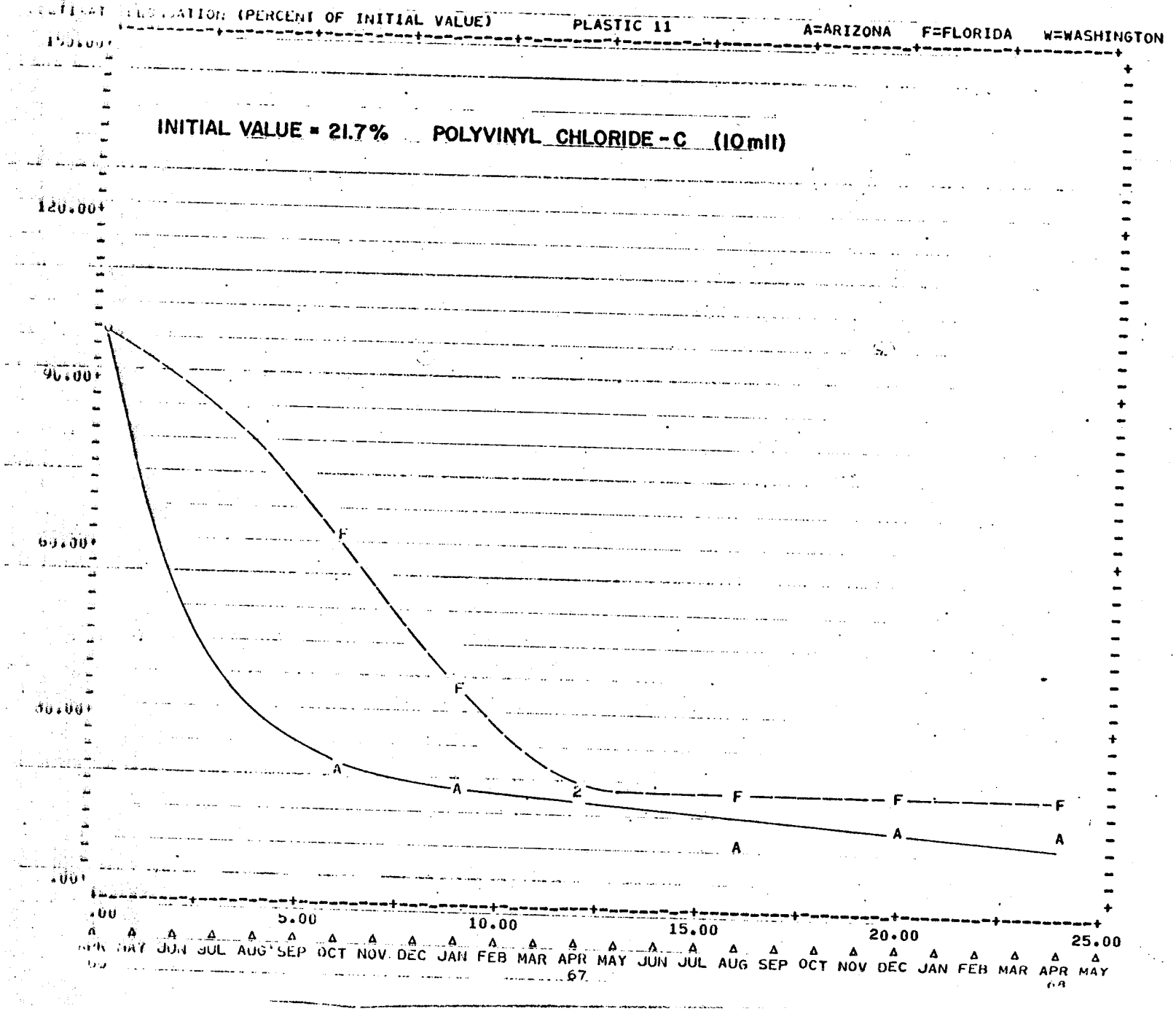

(PERCENT OF INITIAL VALUE)
PLASTIC 11
A=ARIZONA F=FLORIDA W=WASHINGTON
INITIAL VALUE = 21.7% POLYVINYL CHLORIDE - C (10 mil)
120.00
90.00
5.00
10.00
15.00
20.00
25.00
MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
67

FIGURE 14

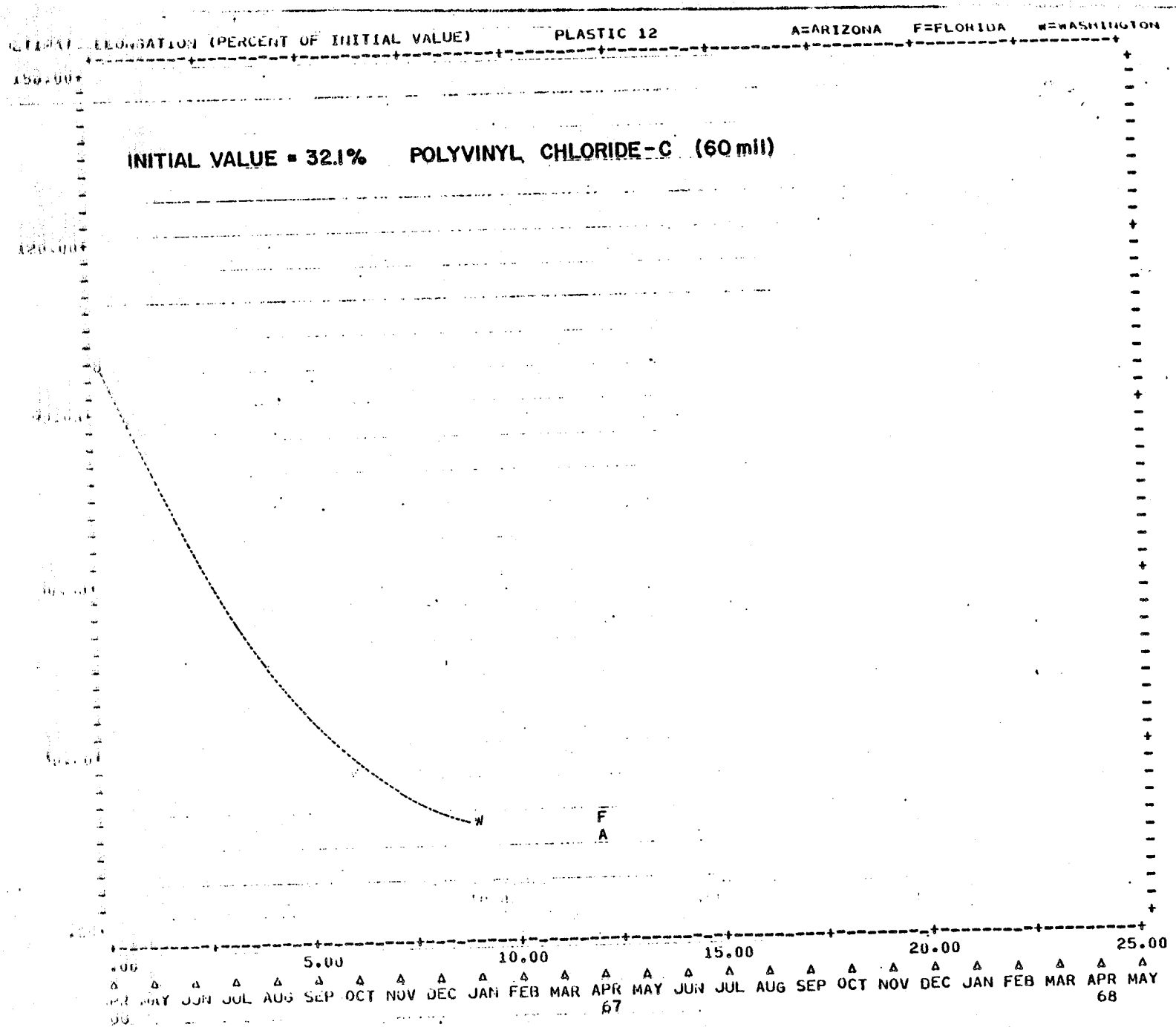

ELONGATION (PERCENT OF INITIAL VALUE)
PLASTIC 12
A=ARIZONA F=FLORIDA W=WASHINGTON
INITIAL VALUE = 32.1% POLYVINYL CHLORIDE-C (60 mil)
W
F
A
5.00
10.00
15.00
20.00
25.00
JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
67
68

FIGURE 15

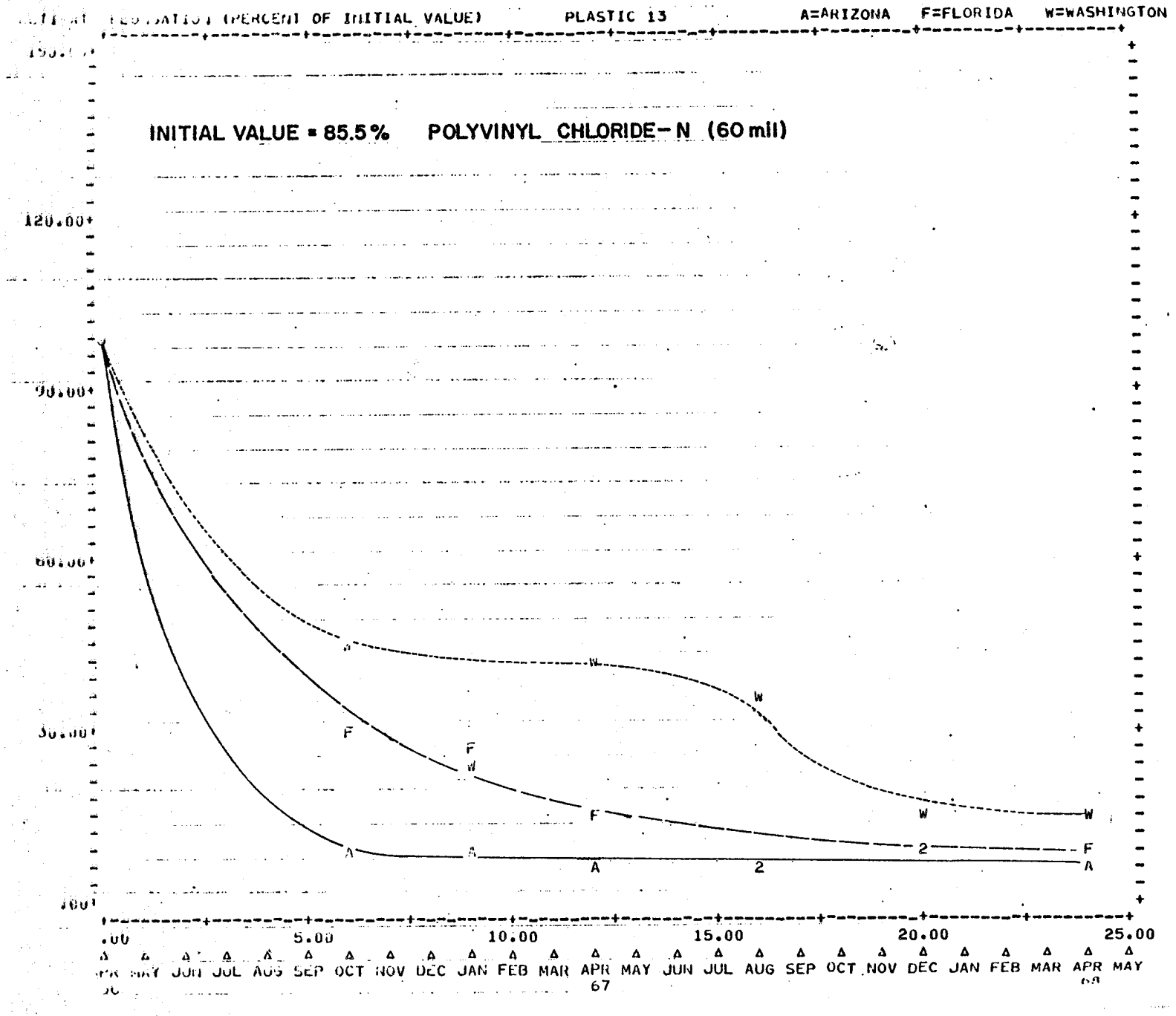

PLASTIC 13
A=ARIZONA F=FLORIDA W=WASHINGTON
INITIAL VALUE = 85.5% POLYVINYL CHLORIDE-N (60 mil)
120.00
90.00
30.00
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
67
68

FIGURE 16

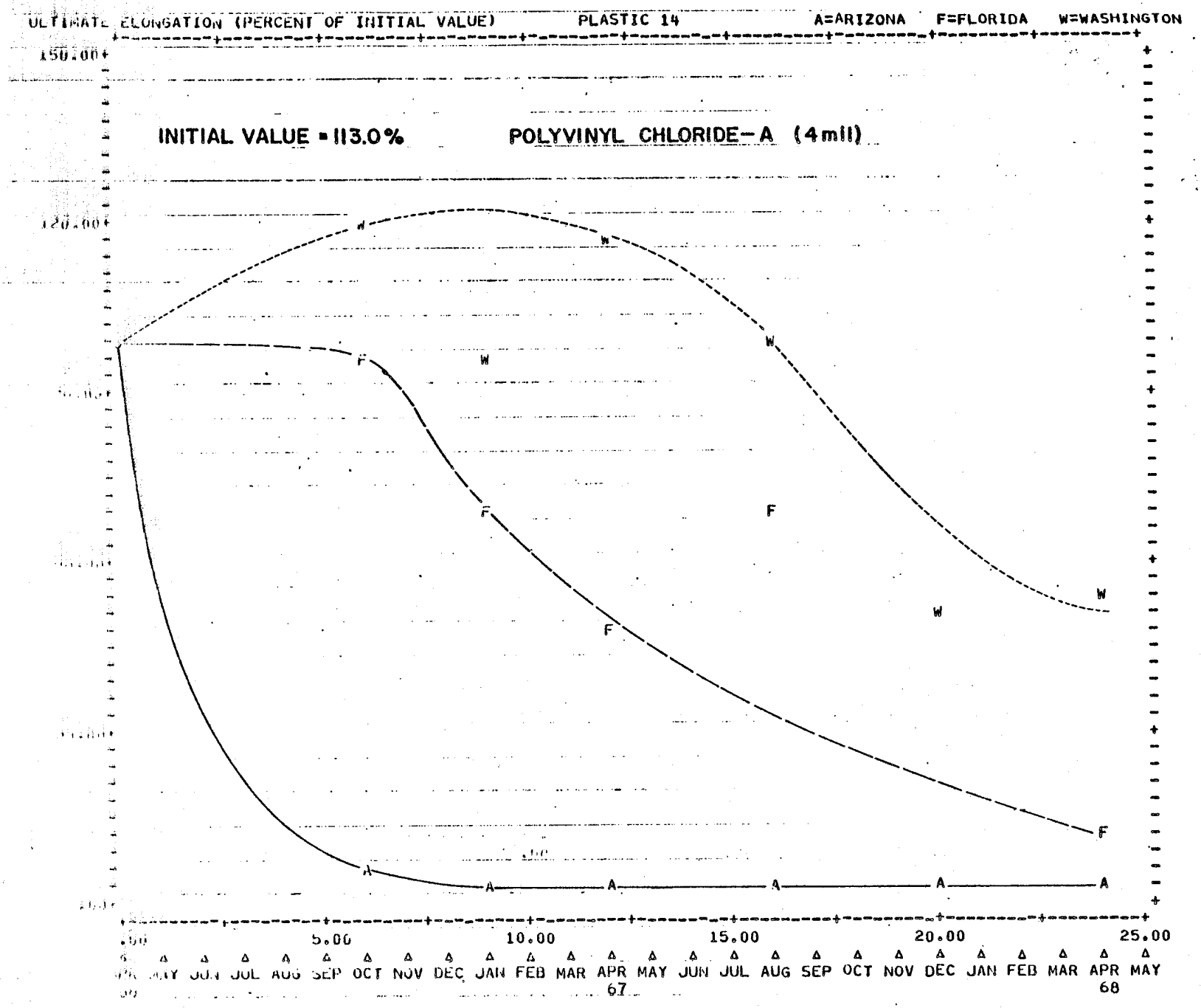

ULTIMATE ELONGATION (PERCENT OF INITIAL VALUE)
PLASTIC 14
A=ARIZONA F=FLORIDA W=WASHINGTON
INITIAL VALUE = 113.0%
POLYVINYL CHLORIDE—A (4mil)
150.00
120.00
5.00
10.00
15.00
20.00
25.00
MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
67
68

FIGURE 17

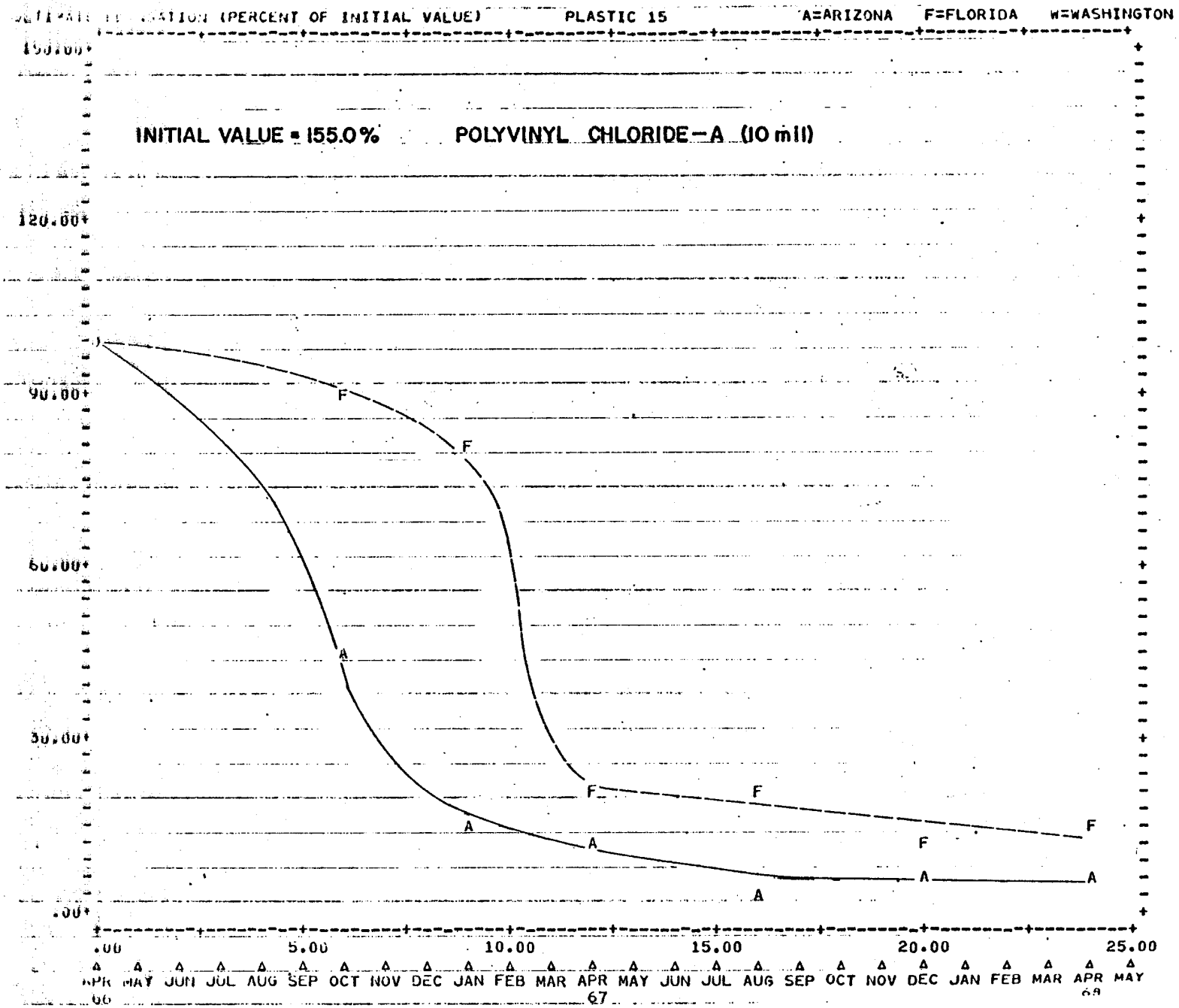

PLASTIC 15
A=ARIZONA F=FLORIDA W=WASHINGTON
INITIAL VALUE = 155.0%
POLYVINYL CHLORIDE—A (10 mil)
120.00
90.00
60.00
30.00
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
66
67
69

FIGURE 18

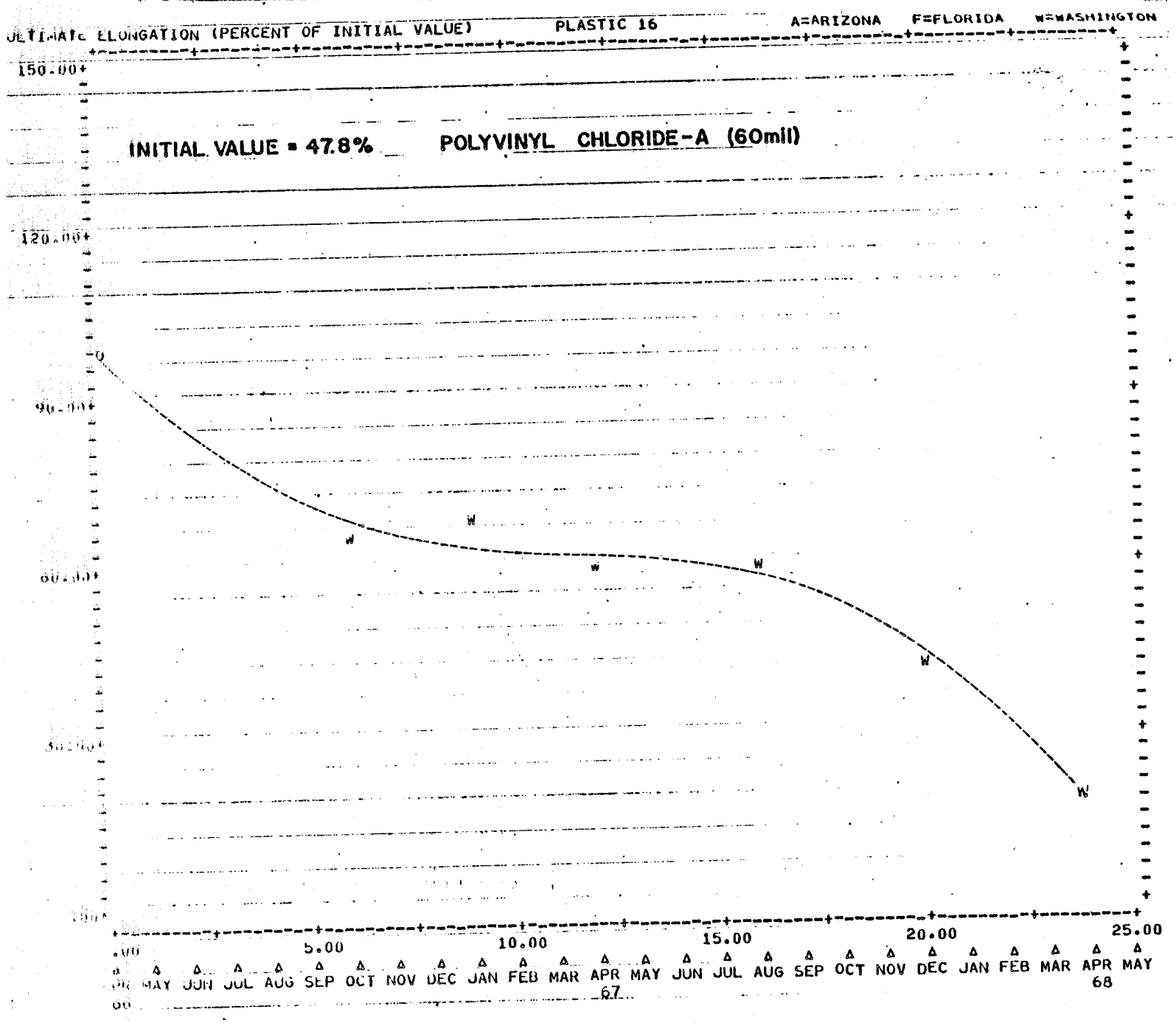

ULTIMATE ELONGATION (PERCENT OF INITIAL VALUE)
PLASTIC 16
A=ARIZONA F=FLORIDA W=WASHINGTON
150.00+
INITIAL VALUE = 47.8%
POLYVINYL CHLORIDE-A (60mil)
120.00+
90.00+
60.00+
30.00+
0
W
5.00
10.00
15.00
20.00
25.00
MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
67
68

FIGURE 19

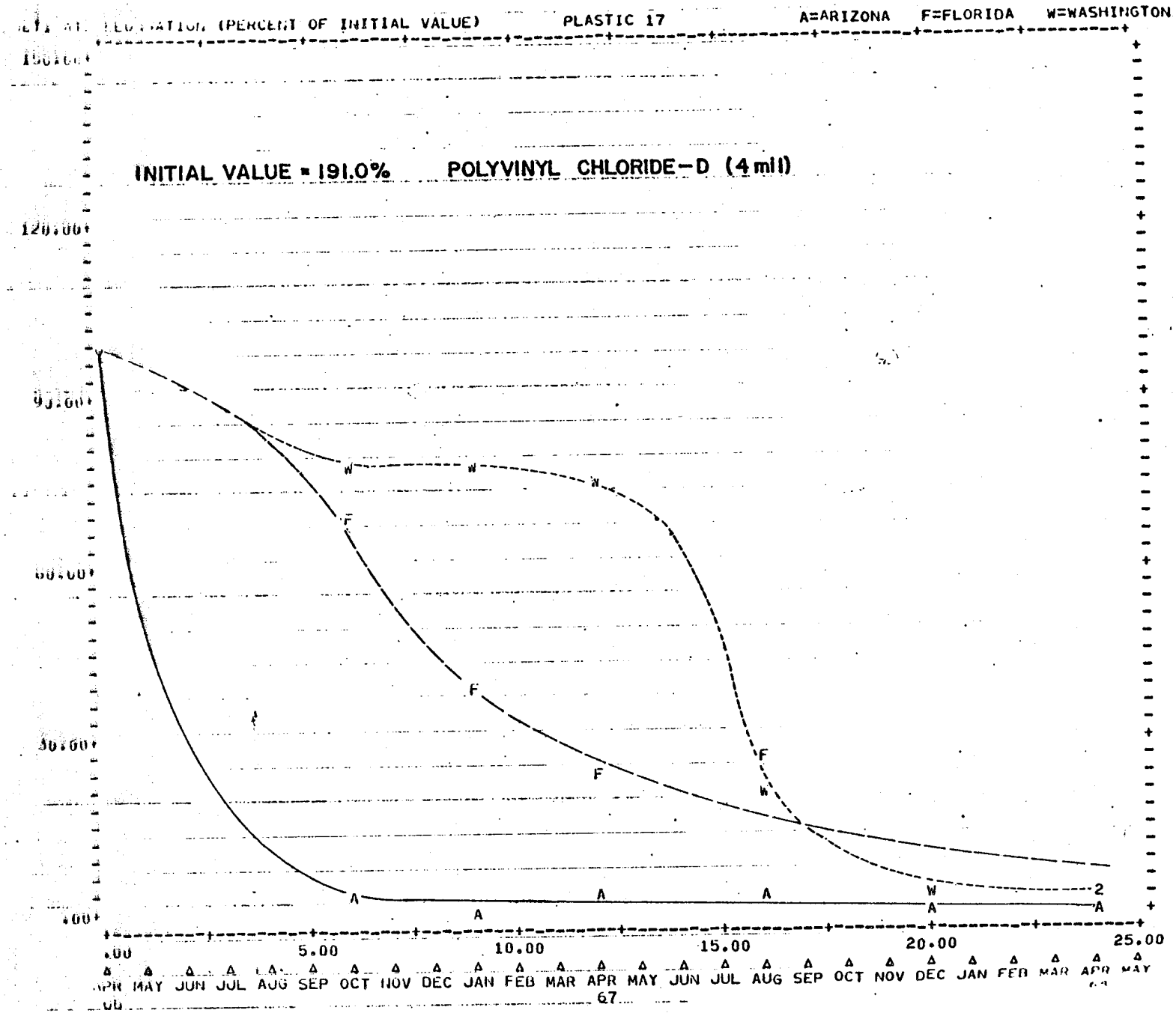

PLASTIC 17
A=ARIZONA F=FLORIDA W=WASHINGTON
INITIAL VALUE = 191.0% POLYVINYL CHLORIDE-D (4 mil)
120.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
67

FIGURE 20

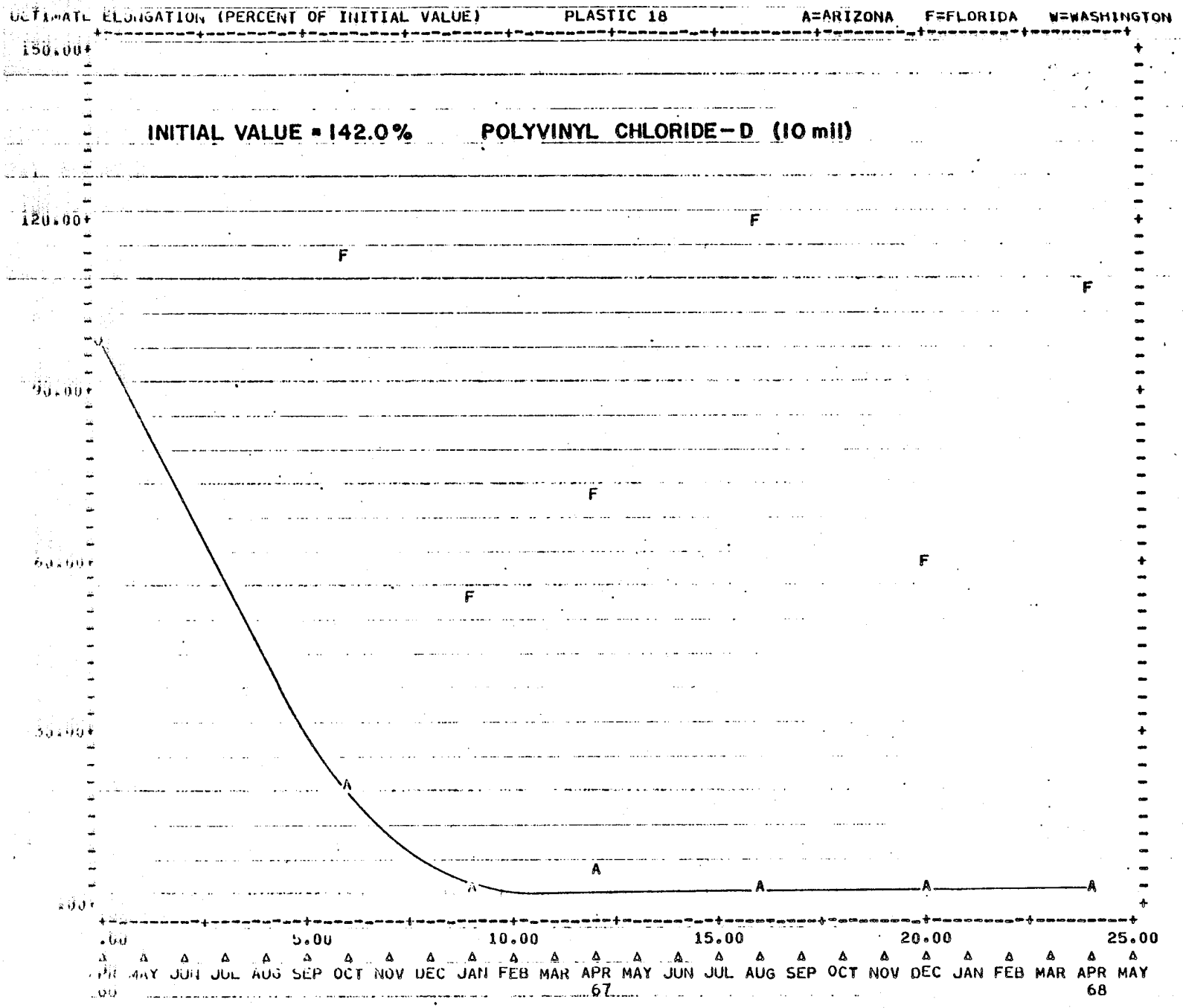

ULTIMATE ELONGATION (PERCENT OF INITIAL VALUE)
PLASTIC 18
A=ARIZONA F=FLORIDA W=WASHINGTON
INITIAL VALUE = 142.0%
POLYVINYL CHLORIDE-D (10 mil)
150.00
120.00
90.00
60.00
30.00
.00
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
67
68

FIGURE 21

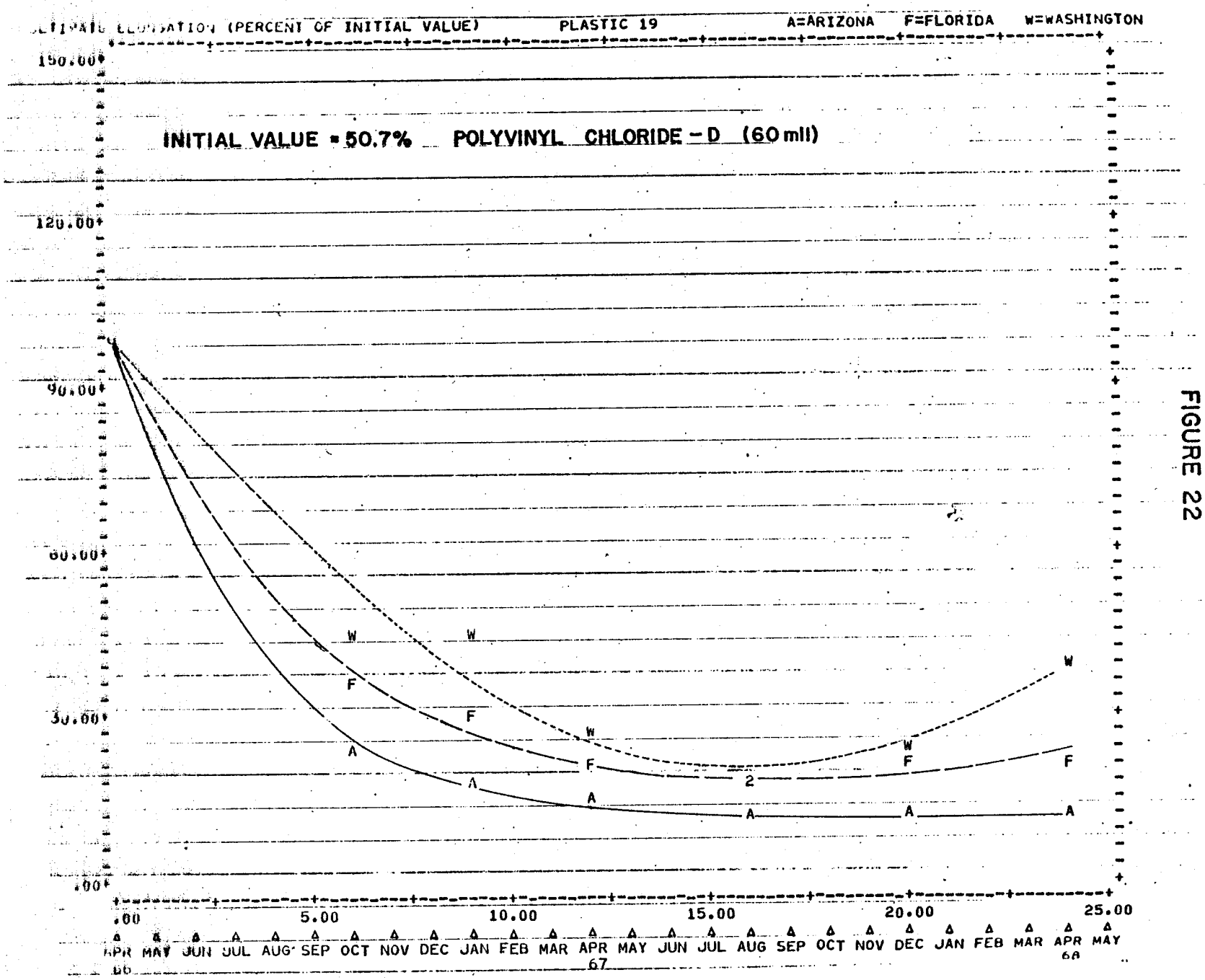

ELONGATION (PERCENT OF INITIAL VALUE)
PLASTIC 19
A=ARIZONA F=FLORIDA W=WASHINGTON
INITIAL VALUE = 50.7% POLYVINYL CHLORIDE - D (60 mil)
150.00
120.00
90.00
60.00
30.00
.00
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
66
67
68

FIGURE 22

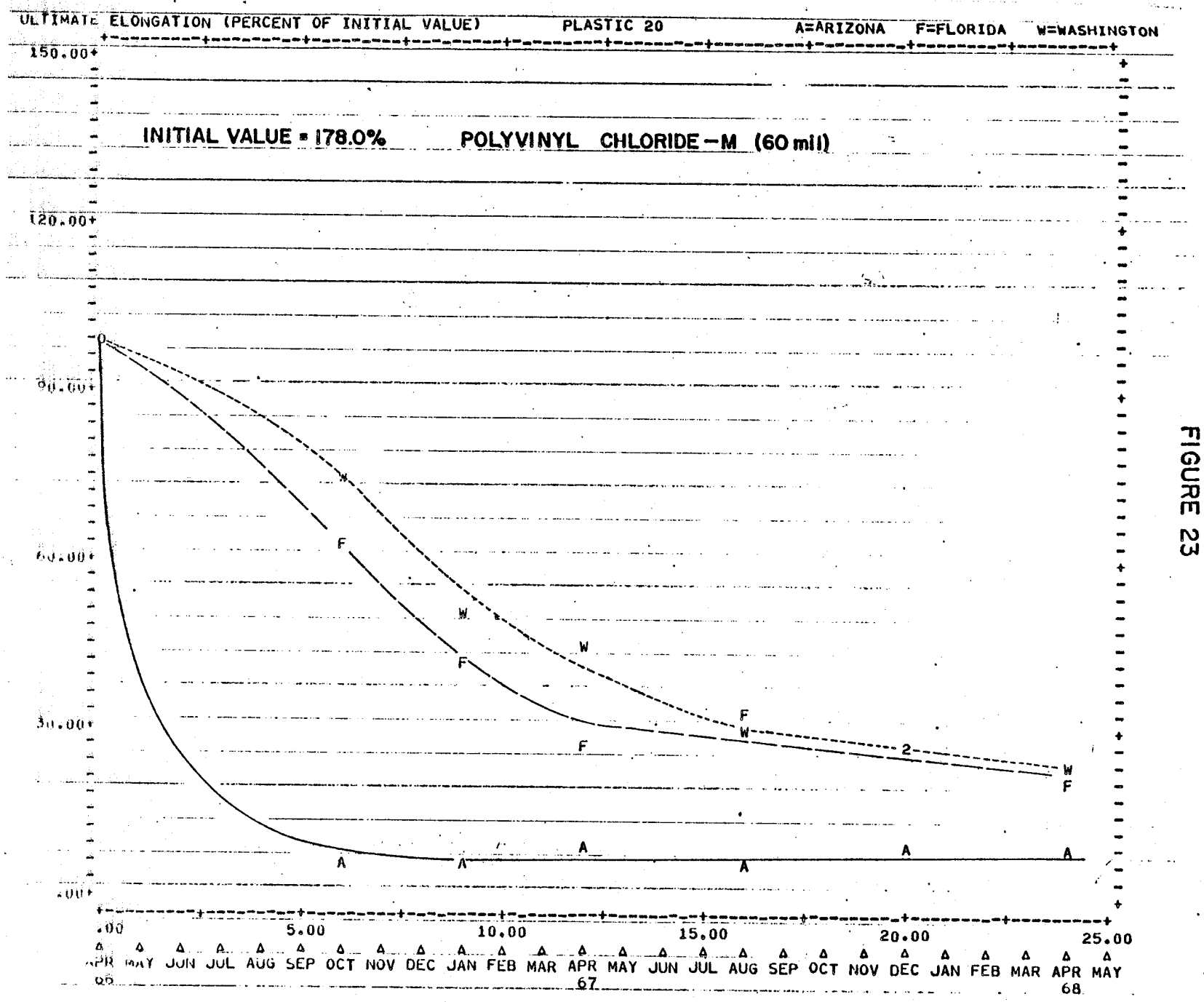

ULTIMATE ELONGATION (PERCENT OF INITIAL VALUE)
PLASTIC 20
A=ARIZONA F=FLORIDA W=WASHINGTON
INITIAL VALUE = 178.0%
POLYVINYL CHLORIDE—M (60 mil)
150.00
120.00
90.00
60.00
30.00
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
66
67
68

FIGURE 23

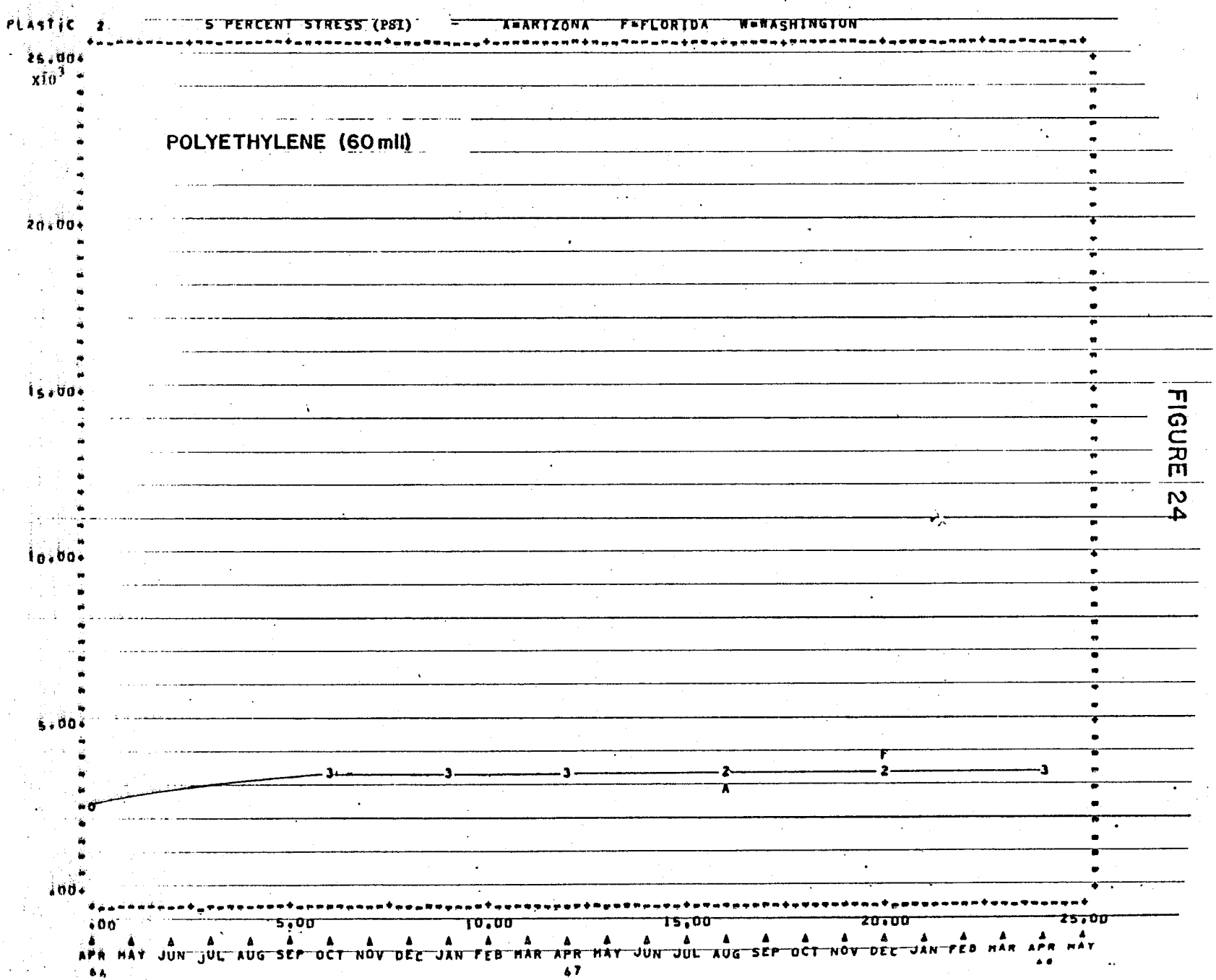

PLASTIC 2
5 PERCENT STRESS (PSI)
A=ARIZONA F=FLORIDA W=WASHINGTON
25.00
X10^3
POLYETHYLENE (60 mil)
20.00
15.00
10.00
5.00
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
64
67
68

FIGURE 24

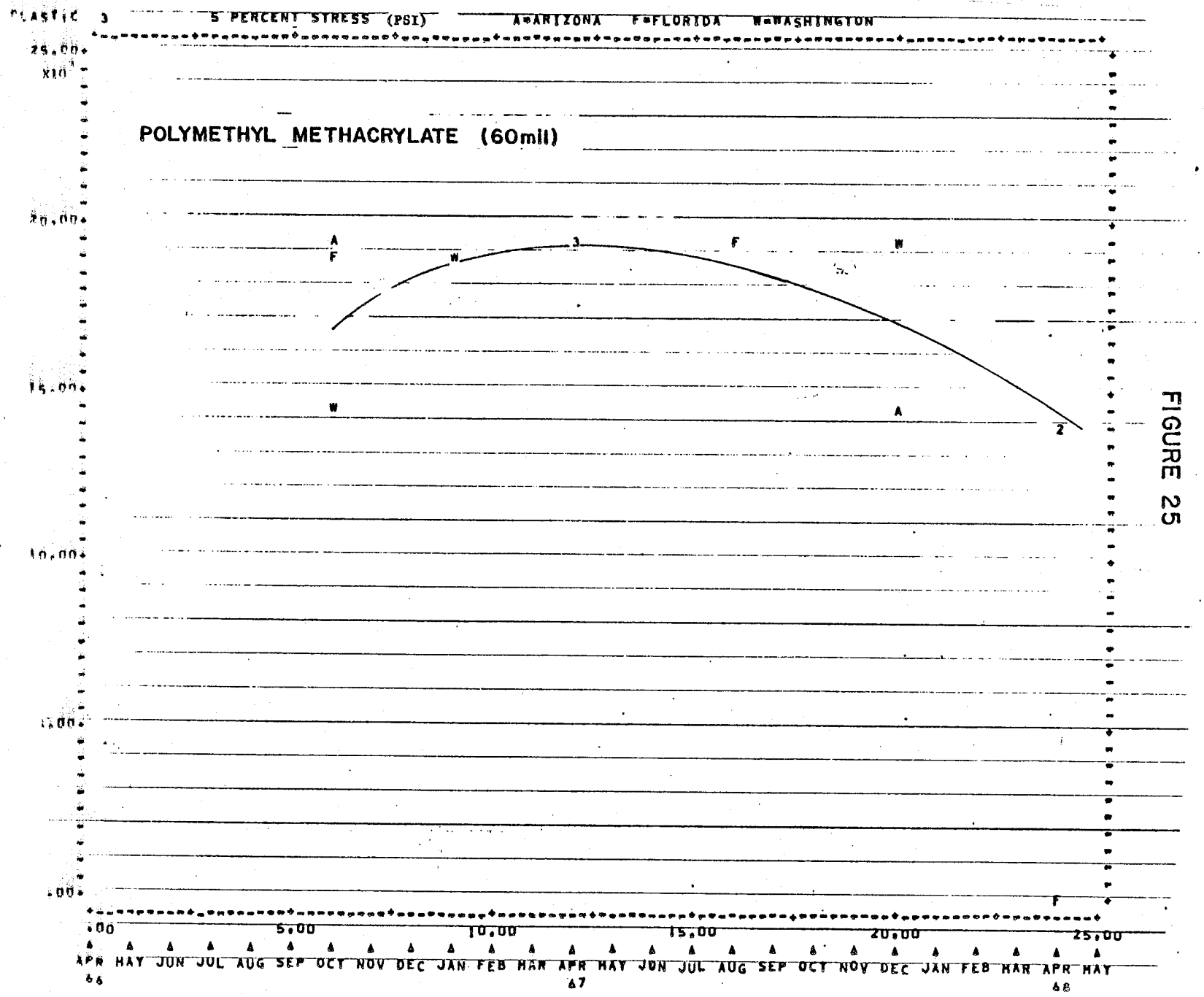

PLASTIC 3
5 PERCENT STRESS (PSI)
A=ARIZONA F=FLORIDA W=WASHINGTON
X10³
25.00
20.00
15.00
10.00
5.00
.00
POLYMETHYL METHACRYLATE (60mil)
A
F
W
3
F
W
W
A
2
F
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
66
67
68

FIGURE 25

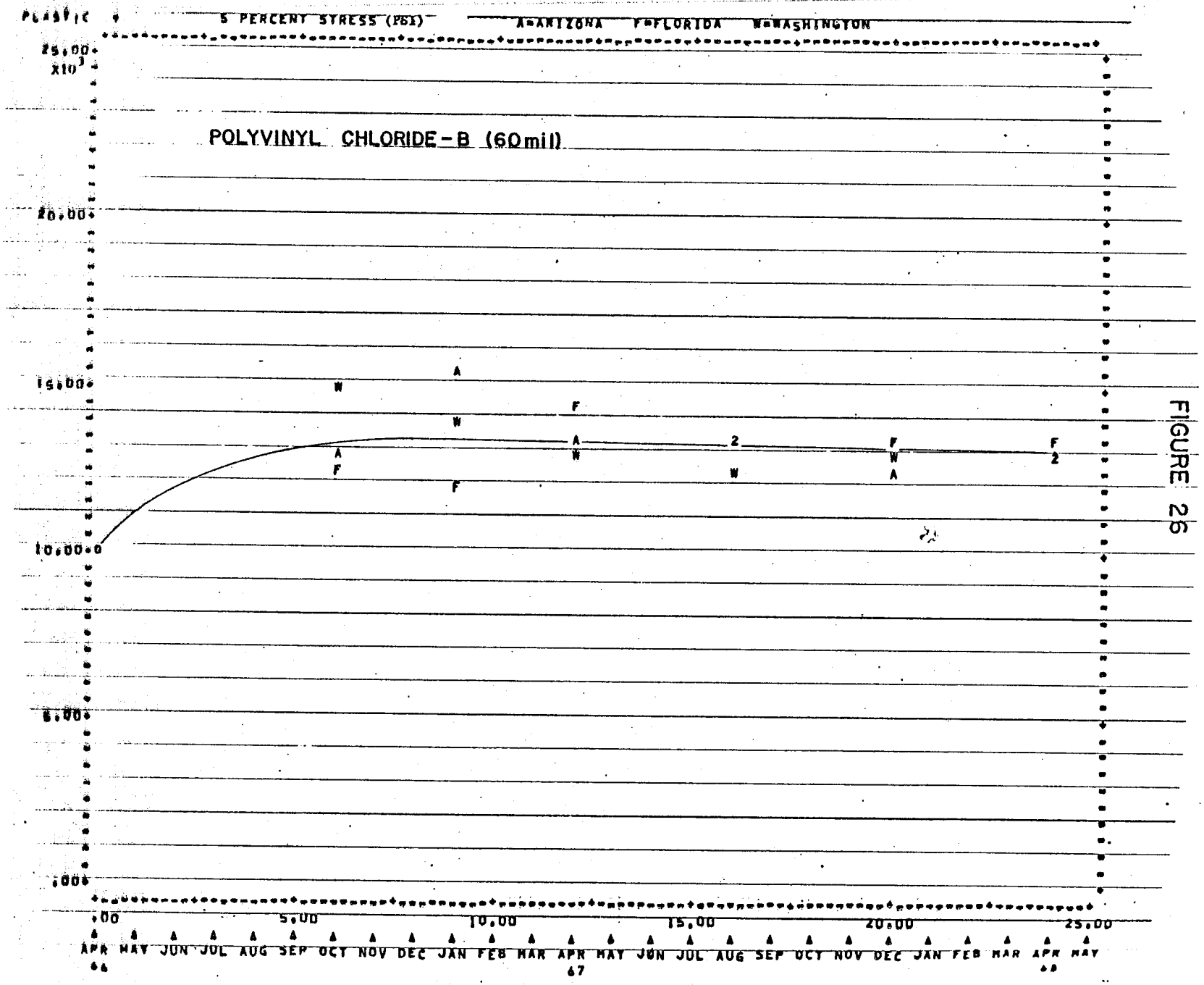

PLASTIC
5 PERCENT STRESS (PSI)
A=ARIZONA F=FLORIDA W=WASHINGTON
25,00
X10³
POLYVINYL CHLORIDE-B (60mil)
20,00
15,00
10,00.0
5,00
,000
,00
5,00
10,00
15,00
20,00
25,00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
66
67
68

FIGURE 26

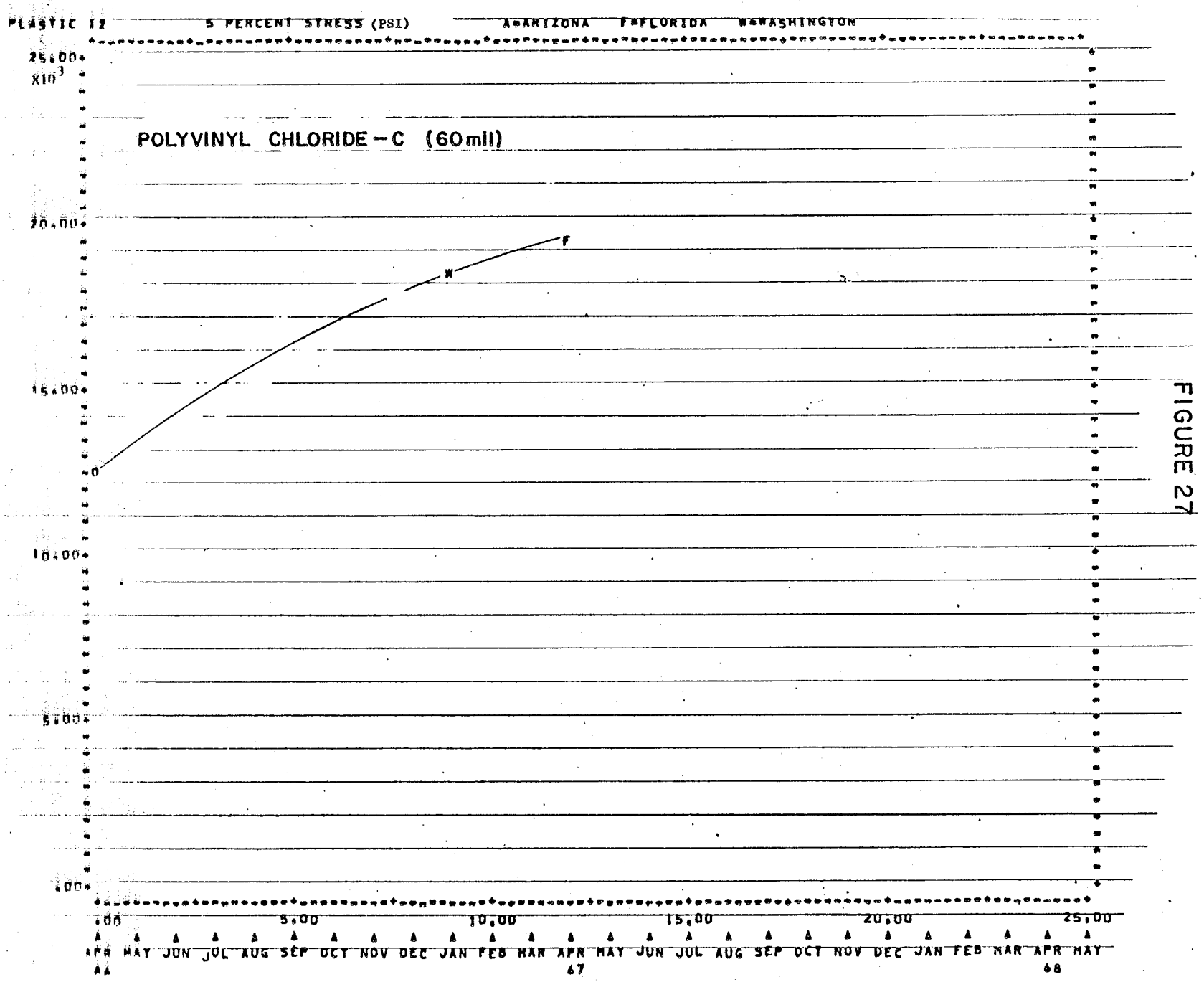

PLASTIC 12
5 PERCENT STRESS (PSI)
A=ARIZONA F=FLORIDA W=WASHINGTON
25.00
X10³
POLYVINYL CHLORIDE – C (60 mil)
20.00
15.00
10.00
5.00
.00
F
W
0
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
66
67
68

FIGURE 27

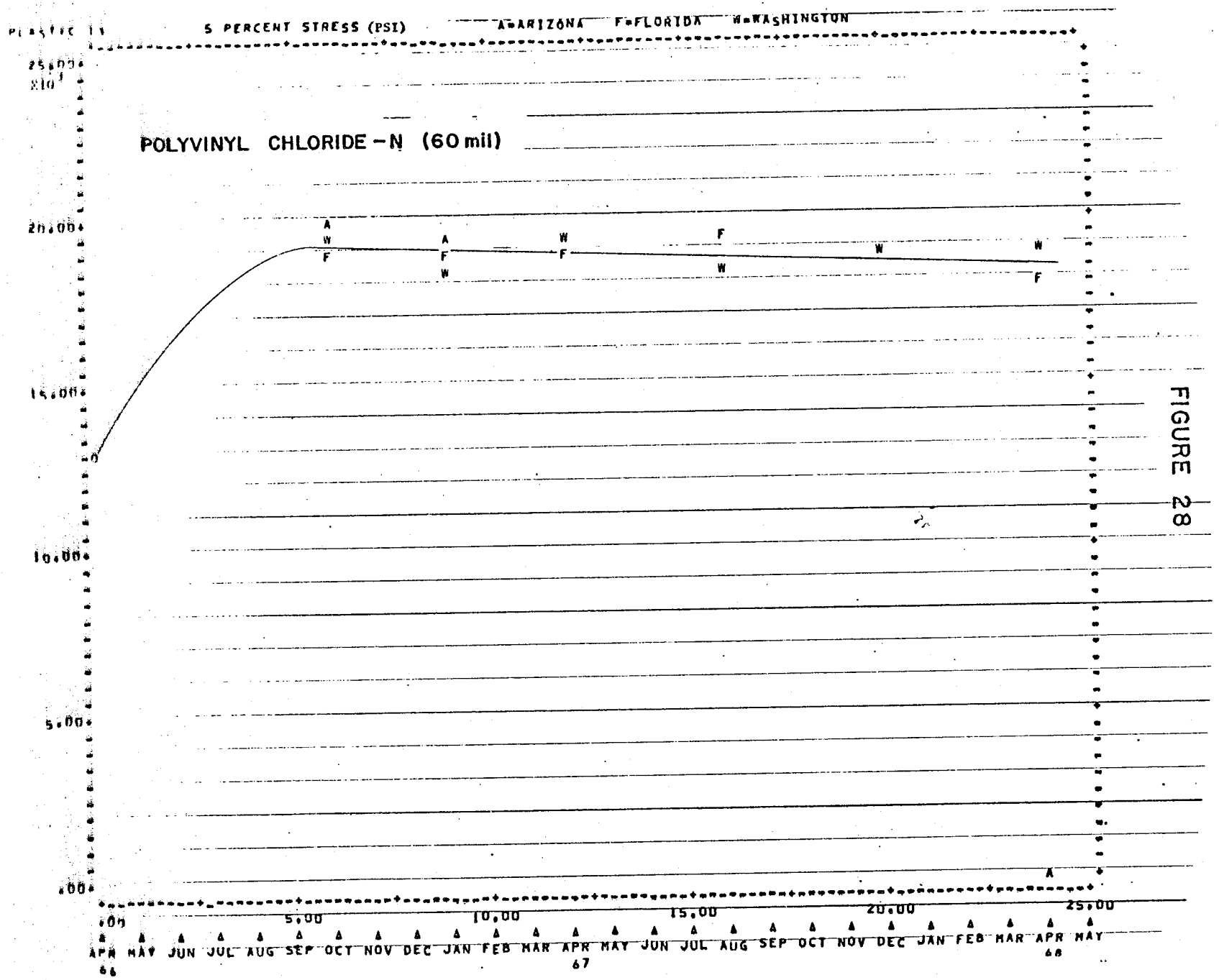

PLASTIC IN
5 PERCENT STRESS (PSI)
A=ARIZONA F=FLORIDA W=WASHINGTON
POLYVINYL CHLORIDE – N (60 mil)
25.00
20.00
15.00
10.00
5.00
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
66
67
68

FIGURE 28

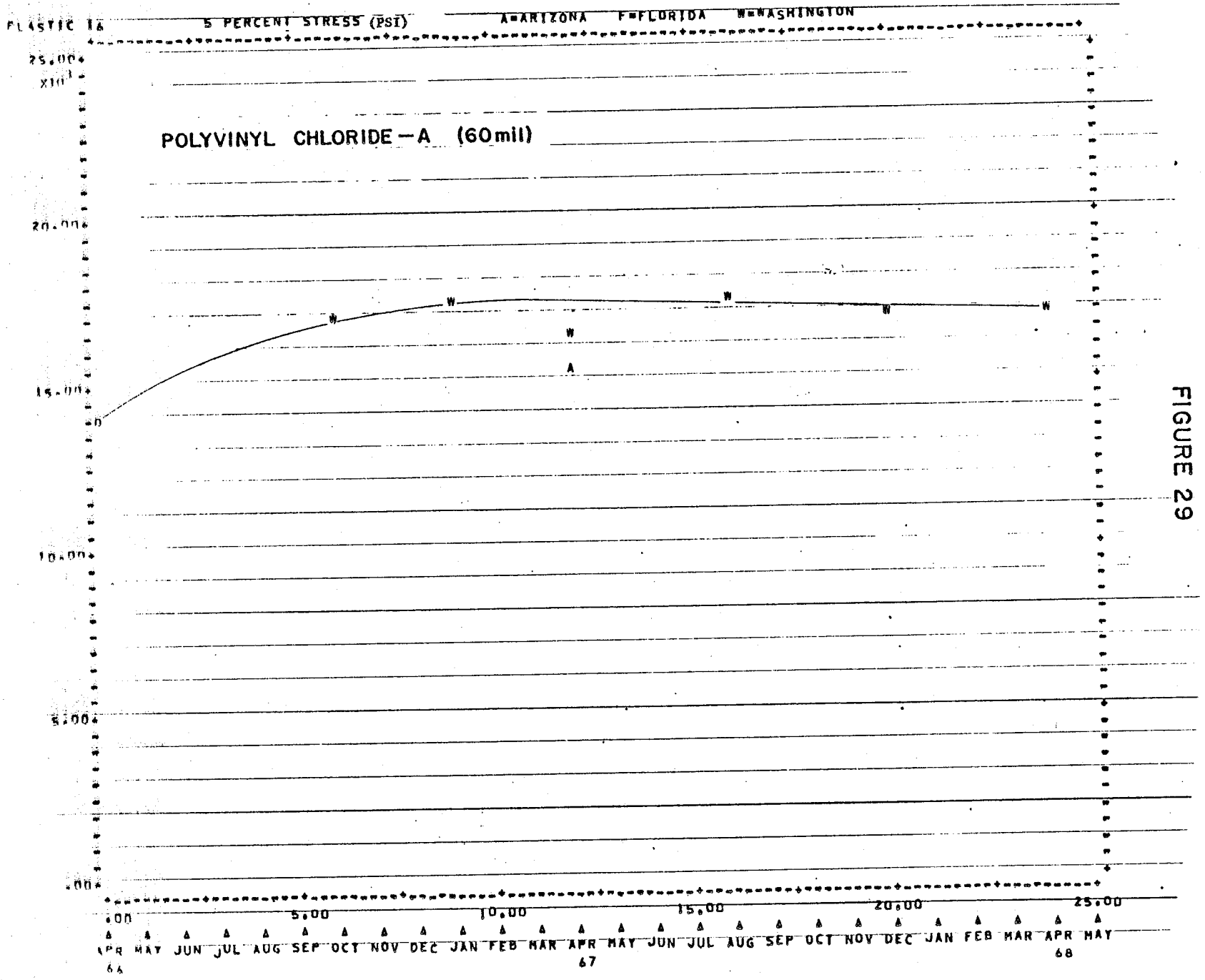

PLASTIC 1A
5 PERCENT STRESS (PSI)
A=ARIZONA F=FLORIDA W=WASHINGTON
X10³
25.00
20.00
15.00
10.00
5.00
.00
POLYVINYL CHLORIDE—A (60mil)
W
W
W
W
W
W
A
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
66
67
68

FIGURE 29

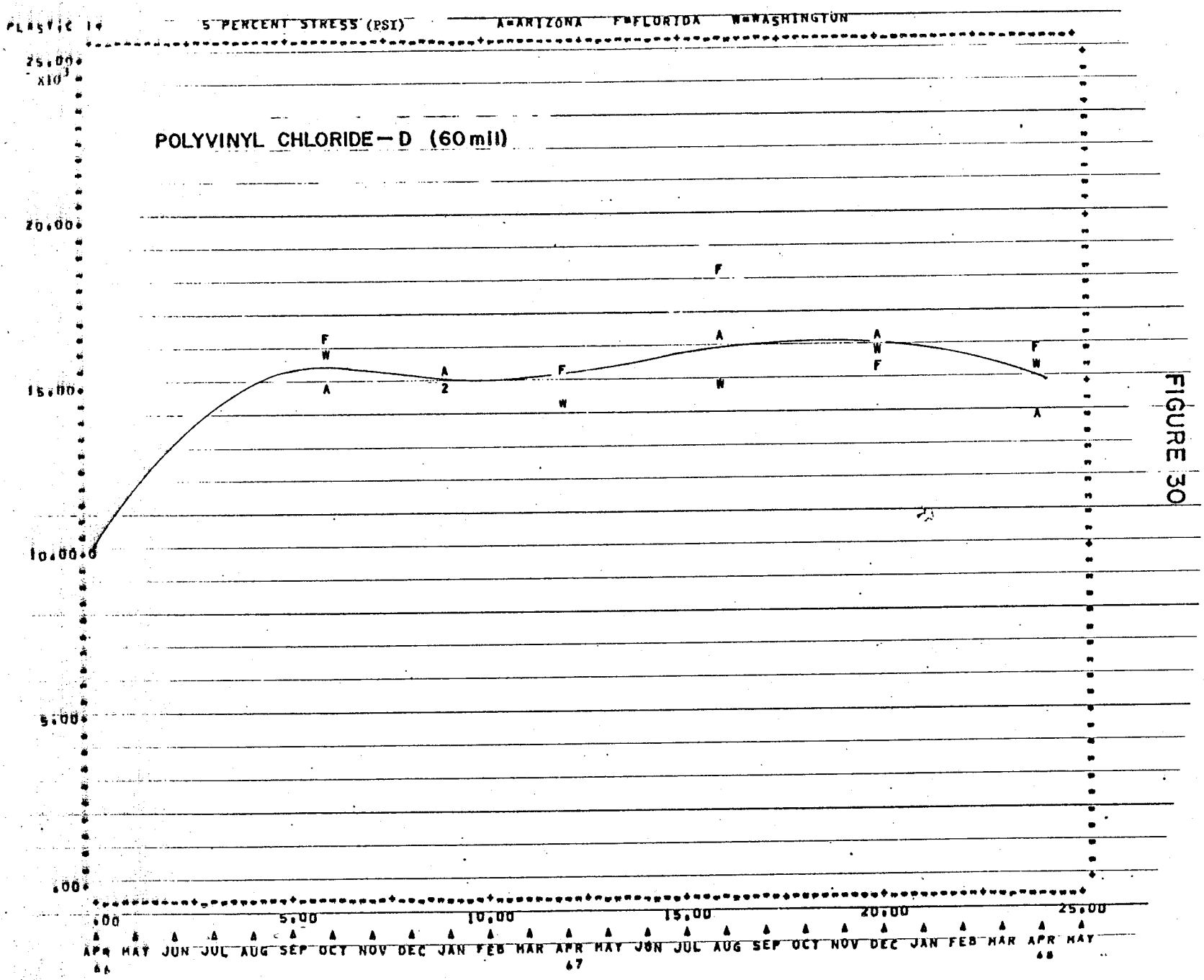

PLASTIC I
5 PERCENT STRESS (PSI)
A=ARIZONA F=FLORIDA W=WASHINGTON
25.00
X10³
POLYVINYL CHLORIDE—D (60 mil)
20.00
15.00
10.00
5.00
.00
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
66
67
68

FIGURE 30

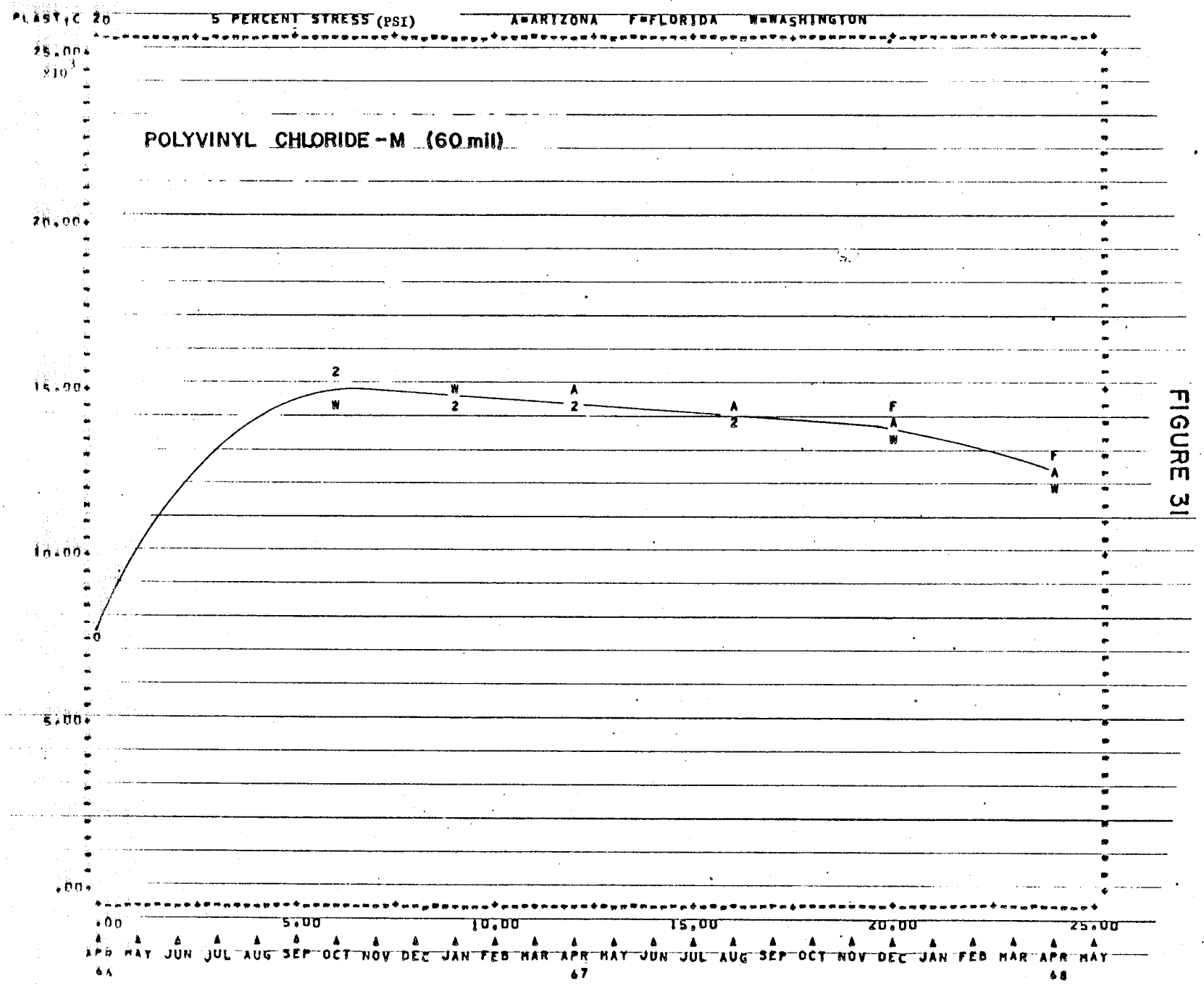

PLASTIC 20
5 PERCENT STRESS (PSI)
A=ARIZONA F=FLORIDA W=WASHINGTON
POLYVINYL CHLORIDE-M (60 mil)
25.00
20.00
15.00
10.00
5.00
.00
0
2
W
W
2
A
2
A
2
F
A
W
F
A
W
.00
5.00
10.00
15.00
20.00
25.00
APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY
66
67
68

FIGURE 31

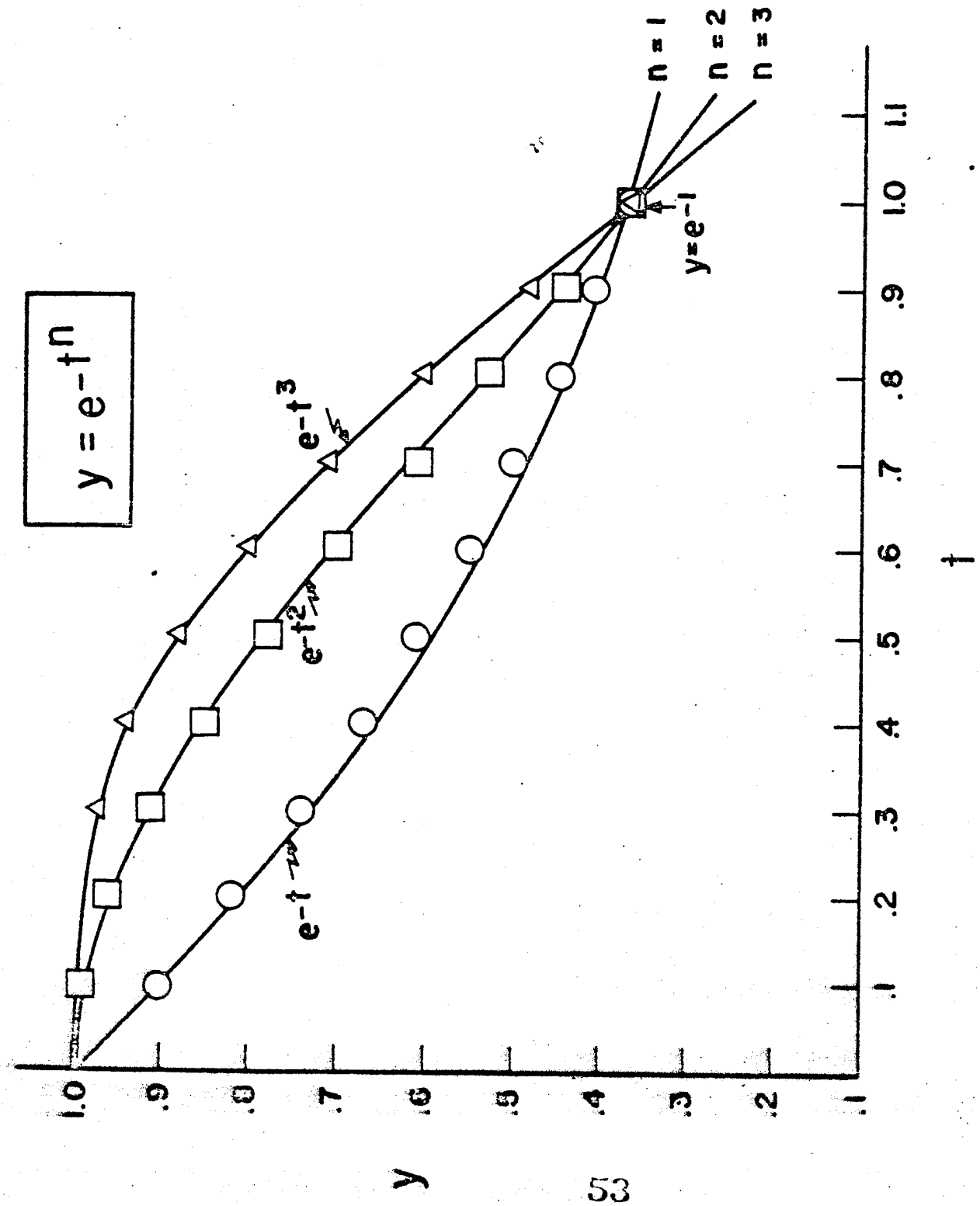



FIGURE 32